İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

THERMODYNAMIC ANALYSIS OF POLY(N-ISOPROPYLACRYLAMIDE) NETWORK-LINEAR POLYMER-SOLVENT SYSTEMS

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DOKÜMANTASYON MERKEZİ

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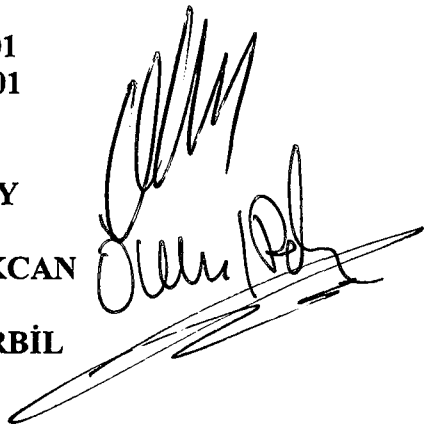

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T.C. YÜKSEKÖĞRETİM KURULU DOKÜMANTASYON MERKEZİ

TABLE OF CONTENTS

LIST OF SYMBOLS

a_i	: Activity of component i
A, B	: Lower and upper critical points on the phase boundary
A	: Ion pairing coefficient
f	: Effective charge density of the network
f_0	: Charge density of the network
ΔG	: The change in the Gibbs free energy
ΔG_m	: Gibbs free energy change of mixing
ΔG_{el}	: Gibbs free energy change of elastic deformation
ΔG_i	: Gibbs free energy change of electrostatic interaction
$\Delta \overline{G}_i$	: Partial molar Gibbs free energy of the species i
ΔH	: Enthalpy change
ΔH_m	: Enthalpy change of mixing
k	: Boltzmann constant
n_1, n_2, n_3	: Number of moles of solvent, polymer network and linear polymer
N	: Crosslink density of gel
N_A	: Avogadro's number
N_0	: Total number of lattice sites
N_1, N_2	: Total number of solvent and solute molecules in a solution
R	: The gas constant
ΔS_m	: Entropy change of mixing
ΔS_m^{conf}	: Configurational entropy change of mixing
$\overline{X}_n$	: Number average degree of polymerization
x	: Number of segments of a polymer chain
x_1, x_2	: Mole fractions of solvent and solute molecules in a solution
T	: Absolute temperature (K)
T_C	: Critical solution temperature
V_1	: Molar volume of solvent
V_2	: Molar volume of polymer
$\Delta\mu_1, \Delta\mu_2, \Delta\mu_3$	: Change in the chemical potential of solvent, polymer network and linear polymer
$\Delta\mu_i^{gel}$	: Change in the chemical potential of component i in gel phase
$\Delta\mu_i^{sol}$	: Change in the chemical potential of component i in solution phase
ν_i	: Number of ways of arranging th i-th polymer molecule on a lattice to which i-1 polymer molecules have been added previously
ν_1	: Volume fraction of solvent

T.C. YÜKSEKÖĞRETİM KURULU
DOKÜMANTASYON MERKEZİ

v_2 : Volume fraction of polymer network at equilibrium degree of swelling

v_2^0 : Volume fraction of polymer network after gel preparation

v_3 : Volume fraction of linear polymer

v_3/ϕ : Partition parameter of linear polymer

W_{ij} : Interaction free energy associated with the formation of a contact between a pair of segments of molecules i and j

y : Number of segments in linear polymer

z : Coordination number of a lattice

α : Equilibrium swelling ratio

α_s : Factor expressing the linear deformation of a network structure by isotropic swelling

$\alpha_x, \alpha_y, \alpha_z$: Linear deformation factor with reference to x,y and z coordinates

θ : Theta temperature

π : Osmotic pressure

χ_1 : Parameter expressing the first neighbor interaction free energy, divided by kT, for solvent with polymer

χ_{12} : Interaction parameter between solvent and polymer network

χ_{13} : Interaction parameter between solvent and linear polymer

χ_{23} : Interaction parameter between polymer network and linear polymer

ϕ : Volume fraction of linear polymer in external solution

Φ : Average functionality

Ω : Total number of conformations

LIST OF FIGURES

THERMODYNAMIC ANALYSIS OF POLY(N-ISOPROPYLACRYLAMIDE) NETWORK-LINEAR POLYMER-SOLVENT SYSTEMS

SUMMARY

Many studies have been reported in the literature on the swelling behavior of hydrogels in low molecular weight solvents. However, only a few were concerned with the swelling behavior of hydrogels in aqueous solution of linear polymers.

In the present work, a detailed thermodynamic analysis of the (quasi)ternary system consisting of poly(N-isopropylacrylamide) (PNIPA) network, linear polymer, and solvent (water) was carried out. The classical Flory-Huggins (FH) theory was used to derive the equations for the free energy of the system as well as the chemical potential of the components. The chemical potential equations were solved for the equilibrium swelling state of the system. The state of equilibrium swelling of a network immersed in a polymer solution was obtained when the solvent and the polymer inside the network are in thermodynamic equilibrium with those outside. This equilibrium state was described by the equality of the chemical potential of these components in both phases. The system of equations describing the thermodynamic equilibrium condition of the system was solved to calculate the following parameters;

1) Volume of PNIPA gel in linear polymer solutions ($1/\nu_2$).
2) Partition parameter of the linear polymer between the inside and outside of the gel phase (ν_3/ϕ).

For these calculations, the required values of the interaction parameters were taken to be very close to the typical experimental parameters reported in the literature. General results were obtained illustrating the effects of the temperature of the system, the extent of the interactions between the components on the volume of PNIPA gel as well as on the linear polymer distribution coefficient.

The calculation results indicated that PNIPA gels exhibit reentrant phase transition in linear polymer solutions. In such a transition, the gel first collapses then reswells if a particular external parameter such as the linear polymer concentration is continuously varied. The necessary condition for the reentrant behavior of PNIPA gels was predicted in terms of the interaction parameters between the PNIPA network, linear polymer and solvent as $\chi_{13} \cong 0$, $\chi_{23} = 0$. It was shown that the linear polymer molecules attracted both by solvent and by PNIPA gel that are responsible for the observed reentrant phase transition behavior. The linear polymer first flows from the gel to the solution phase due to the attractive interactions between the segments of the linear polymer and solvent but then reenter the gel phase at higher

polymer concentration due to the attractive interactions between the linear polymer and PNIPA gel.

The effect of temperature on the swelling behavior of PNIPA gels for different values of the linear polymer-solvent interaction parameter (χ_{13}) was also investigated. It was found that, as the quality of the solvent for the linear polymer becomes worse, reentrant phase transition in PNIPA gels can be induced by increasing the temperature. Calculations were also carried out to determine the effect of the extent of the linear polymer-PNIPA interactions represented by χ_{23}. It was observed that increasing the compatibility between the segments of the linear polymer and PNIPA promotes the occurrence of reentrant phase transition in PNIPA gels.

POLİ(N-İZOPROPİLAKRİLAMİD) AĞYAPI-LİNEER POLİMER VE ÇÖZÜCÜ SİSTEMLERİNİN TERMODİNAMİK ANALİZİ

ÖZET

Hidrojellerin düşük molekül ağırlıklı çözücülerde şişme davranışlarının incelenmesi konusunda yoğun araştırmalar yapılmasına karşın, polimer çözeltileri içindeki şişme davranışları konusunda çok az çalışma yayınlanmıştır.

Bu çalışma kapsamında, PNİPA jellerinin polimer çözeltileri içindeki davranışlarının anlaşılması için PNİPA ağyapı, lineer polimer ve çözücüden oluşan tersiyer sistemlerin detaylı bir termodinamik analizi yapılmıştır. Flory-Huggins (FH) teorisi kullanılarak, PNİPA ağyapı- lineer polimer- çözücü komponentlerinden oluşan iki fazlı sistemdeki serbest enerji ve ayrıca kimyasal potansiyel değişimlerini veren denklemler türetilmiştir. Sistemde şişmenin dengeye ulaştığı an için, kimyasal potansiyel denklemleri çözülmüştür. Polimer çözeltisindeki bir jelin şişme dengesine ulaşması, jel içindeki çözücü ve lineer polimer aktivitesinin dış çözeltilerdekiler ile denge halinde olmasına bağlıdır. Sistem şişme dengesine ulaştığında, herbir bileşenin polimer ağyapı (jel) içinde ve dışındaki çözeltide kimyasal potansiyelleri eşittir. Bu denge anı için kimyasal potansiyel denklemleri çözülerek, PNİPA jellerinin polimer çözeltileri içindeki davranışlarını belirleyen parametreler hesaplanmıştır;

1) PNİPA jelindeki hacim değişmeleri ($1/\nu_2$).
2) Lineer polimer moleküllerinin jelin içindeki ve dışındaki çözeltide dağılım katsayısı (ν_3/ϕ).

Bu değerlerin hesaplanması için gerekli PNİPA-çözücü, PNİPA-lineer polimer ve çözücü-lineer polimer etkileşim parametreleri, literatürde verilen deneysel çalışmalardaki değerlere çok yakın seçilmiştir. PNİPA jelinin lineer polimer çözeltileri içindeki faz geçişlerine ait teorik sonuçlar, tersiyer sistem üzerine sıcaklığın, lineer polimerin molekül ağırlığının, sistemin bileşenleri arasındaki etkileşimlerin ve ayrıca polimer ağyapı içindeki iyonik grupların oluşturduğu etkiler incelenerek elde edilmiştir. Teorik hesaplar sonucunda, dış uyarımlar karşısında (örneğin; dış çözeltideki lineer polimer konsantrasyonu) PNİPA jelinin şişmiş halden büzülmüş hale ve daha sonra tekrar şişmiş hale geçerek reentrant faz geçişi gösterdiği tespit edildi ve bu geçişin gözlenmesi için gerekli koşullar tersiyer sistemin bileşenleri arasındaki etkileşim parametrelerine bağlı olarak belirlendi; $\chi_{13} \cong 0$ ve $\chi_{23} = 0$ olduğunda tersiyer sistemdeki lineer polimer molekülleri hem çözücü ve hem de PNİPA jeli tarafından çekilir ve sistemdeki birbiriyle yarışan bu kuvvetler, jelin reentrant faz geçişi göstermesine neden olur. Lineer polimer moleküllerinin çözücü tarafından çekilmeleri daha baskın olduğunda jel fazından çözelti fazına doğru akarlarken, PNİPA tarafından uygulanan çekimin daha baskın olması sonucunda da tekrar jel fazına girerler.

Lineer polimer ve çözücü arasındaki etkileşim parametresindeki değişimlere bağlı olarak PNİPA jelinin şişme davranışına sıcakılığın etkisi incelendi ve lineer polimer kendisi için ne kadar kötü bir çözücü içinde ise yani; χ_{13} parametresi arttıkça reentrant faz geçişinin gözlendiği sıcaklığında arttığı belirlendi. Ayrıca lineer polimer ve PNİPA ağyapı arasındaki etkileşimin şişmeye etkisini belirlemek için yapılan hesaplar sonucunda, lineer polimer molekülleriyle PNİPA ağyapı arasındaki etkileşimi iyileştirmekle de jelin ani faz geçişi gösterdiği tespit edildi.

1. INTRODUCTION

A gel is a form of matter intermediate between a solid and a liquid[1]. Thus, it has both liquid-like and solid-like properties. The liquid-like properties result from the fact that the major constituent of gels is usually a liquid, e.g. water. It consists of polymers, or long chain molecules to create an infinite three-dimensional network. The liquid prevents the polymer network from collapsing into a compact mass; the network prevents the liquid from flowing away. Depending on chemical composition and other factors, gels vary in consistency from viscous fluids to fairly rigid solids.

Polymer gels are known to exist in two distinct phases, swollen and collapsed. In dried state, a gel is a solid material. However, it swells until it reaches the swelling equilibrium when a solvent is added. Figure 1.1 shows schematically the two states of gels: the collapsed and swollen states.

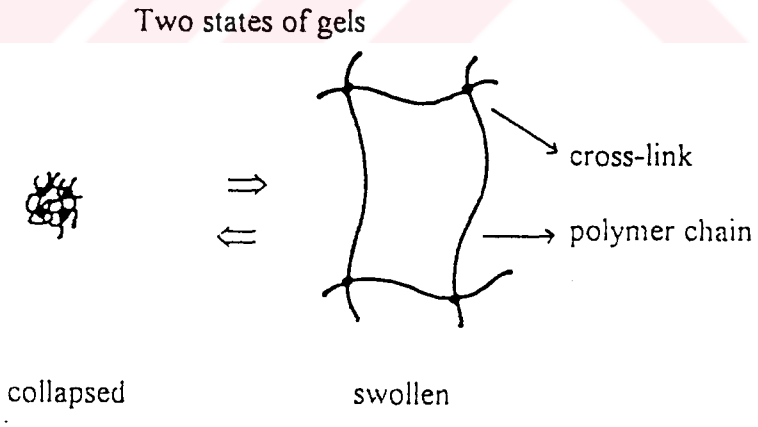

Figure 1.1 Schematic representation of gels in collapsed and swollen states

Drastic changes in the state of the gel can be brought about by small changes in the external conditions. Continuous, discontinuous and also reentrant volume phase transitions occur between the phases in response to chemical and physical stimuli such as temperature, pH, electric field, radiation of UV or visible light, solvent composition and salt concentration[2,3]. For example, when the temperature is lowered, the polymer network loses its elasticity and therefore becomes increasingly compressible. When a certain critical temperature is reached, the elasticity falls to zero and the compressibility becomes infinite. For a gel to undergo the phase transition, it is necessary that polymers interact with each other through both repulsive and attractive interactions and the balance of competing interactions has to be modified by various stimuli. The phase behavior of a gel, therefore, crucially depends on the nature of interactions between polymers.

The study of phase transition of gels was initiated by the theoretical prediction of Dusek and Patterson in 1968[4]. They predicted the possibility of a discontinuous volume change of a gel. Their study led to the prediction that a swollen network phase in equilibrium with pure solvent may undergo a transition into two phases differing in degrees of swelling. Tanaka[5] and Ilavsky[6] have demonstrated the practical relevance of the theoretical considerations and produced phase diagrams that are in qualitative agreement with the diagrams presented by Dusek et al. The volume-phase transition was experimentally discovered for a partially ionized acrylamide gel in a mixture of acetone and water by Tanaka in 1978[5,7]. Later on, Vasilevskaya and Khokhlov studied theoretically the conformational changes in polymer networks swollen in polymer solutions[8]. They predicted the possibility of a first-order phase transition in polymer network-linear polymer-solvent systems. Ishidao et al investigated the swelling behavior of poly(N-isopropylacrylamide) (PNIPA) gels in aqueous glucose and starch solutions[9]. They observed that the gel absorbs low molecular weight glucose, but excludes high molecular weight starch. Recently, a phenomenon called reentrant swelling transition was observed in PNIPA gels immersed in aqueous solutions of poly(ethylene glycol)s (PEGs) of molecular weights 200 to 400 g/mol[10,11]. In such a transition, the gel first collapses then reswells if a particular external parameter such as the linear polymer (PEG)

concentration is continuously varied. As a consequence, the linear polymer first flows from the gel to the solution phase but then reenter the gel phase at higher polymer concentrations[8,12]. Reentrant phase transitions in PNIPA gels were also observed in solvent mixtures such as water-dimethylsulfoxide[3,13], water-methanol [14], or water-ethanol mixtures [14].

The discovery of a discontinuous volume phase transition in gels, which is often called collapse transition has rendered soft materials technologically useful[15]. The applications of these gels can be utilized in mechanical devices or controlled release delivery and separation systems. PNIPA gels have been employed for the separation of a range of materials such as macromolecules, yeasts, and bacteria from aqueous solutions[16,17]. Concentrating such solutions is important due to the fact that a wide range of biological materials are produced as very dilute solutions. For example, when a shrunken PNIPA gel is added to a dilute high-molecular weight polymer solution, the gel swells and absorbs water and other small molecules while macromolecules such as proteins are not absorbed. After recovering the swollen gel and warming, it shrinks drastically and becomes ready for re-use in the concentration process. In this way, the excluded proteins are recovered in a concentrated solution[16]. In these separation applications, the partitioning of macromolecules between the gel and solution phases is the key factor determining the separation efficiency of PNIPA gels.

The object of this study is to investigate the swelling behavior of PNIPA gels in polymer solutions. For this purpose, a detailed thermodynamic analysis of the (quasi)ternary system consisting of PNIPA network, linear polymer, and solvent was carried out using the Flory-Huggins (FH) theory of swelling equilibrium. The effects of various parameters such as the temperature of the system and the energetic interactions between the components on the volume of PNIPA gels in polymer solutions and on the partitioning of the linear polymers between the gel and the external solution was investigated. The necessary condition for the reentrant behavior of PNIPA gels was calculated in terms of the interaction parameters between the PNIPA network, linear polymer and solvent. Using the theoretical work that follows, we determined the necessary conditions for the separation of macromolecules from aqueous solutions by using the PNIPA hydrogels.

T.C. YÜKSEK ... M KURU...
DOKÜMANTASYON MERKEZİ

2.GENERAL THERMODYNAMIC RELATIONS

The behavior of polymers towards solvents is characteristic and different from that of low molecular weight substances. The size and conformations of dissolved polymer molecules require special theoretical treatment to explain their solution properties. In principle, it is possible to calculate ΔG of a given system by applying statistical mechanics to its relevant physical model. However, this theoretical method encounters many difficulties in complex systems such as polymer solutions since they exhibit very large deviations from ideality. Only at extreme dilutions does the polymer solution conform approximately with ideality. At concentrations exceeding a few percentages, deviations from ideality usually become so great that the ideal law is of little value as a basis for rationally correlating the thermodynamic properties of polymer solutions. In fact, none of the available mathematical expressions for ΔG for polymer solutions are yet fully adequate for predicting phase equilibrium behavior quantitatively.

2.1 Thermodynamics of Ideal Solutions

Ideal solutions are defined as solutions in which Raoult's Law is obeyed and the activity of each component (a_i) is equal to its mole fraction (x_i). In such solutions, the molecules of the solvent and polymer are identical in size and for which the energies of like and unlike molecular interactions are equal. The latter condition leads to athermal mixing (i.e., $\Delta H_m = 0$), which also means that there are no changes in the rotational, vibrational and translational entropies of components upon mixing. Thus, ΔS_m depends only upon the configurational entropy change (ΔS_m^{conf}) which is positive because the number of distinguishable spatial arrangements of the molecules increases when they are mixed.

The configurational entropy can be expressed by placing the N_1 molecules of solvent and N_2 molecules of low molecular weight solute on a lattice of $(N_1 + N_2)$ sites. A two-dimensional representation of such an arrangement is shown schematically in Figure 2.1a. The number of distinguishable arrangements (Ω) or molecular conformations is large but calculable;

$$\Omega = \frac{(N_1 + N_2)!}{N_1! N_2!} \tag{2.1}$$

Since all of these configurations represent states of equal energy, the entropy of mixing which is equal to the configurational entropy can be derived by using Boltzmann relation from statistical thermodynamics[18];

$$\Delta S_m = k \ln \frac{(N_1 + N_2)!}{N_1! N_2!} \tag{2.2}$$

where k is the Boltzmann constant. For large values of N Stirling's approximation can be used to deal with the factorials;

$$\ln N! = N \ln N - N \tag{2.3}$$

Substituting Equation (2.3) into Equation (2.2) leads to;

$$\Delta S_m = -k\left[N_1 \ln x_1 + N_2 \ln x_2\right] \tag{2.4}$$

where x_1 and x_2 are the mole fractions of solvent and solute molecules, respectively. Since the universal gas constant is given by $R = N_A k$, where N_A is the Avogadro's constant, Equation (2.4) becomes;

$$\Delta S_m = -R\left[n_1 \ln x_1 + n_2 \ln x_2\right] \tag{2.5}$$

where n_1 and n_2 are the number of moles of solvent and solute. The conditions for ideal mixing imply that the heat of mixing (ΔH_m) is zero. Thus, since $\Delta G_m = \Delta H_m - T\Delta S_m$, the free energy of mixing is given by;

$$\Delta G_m = RT\left[n_1 \ln x_1 + n_2 \ln x_2\right] \tag{2.6}$$

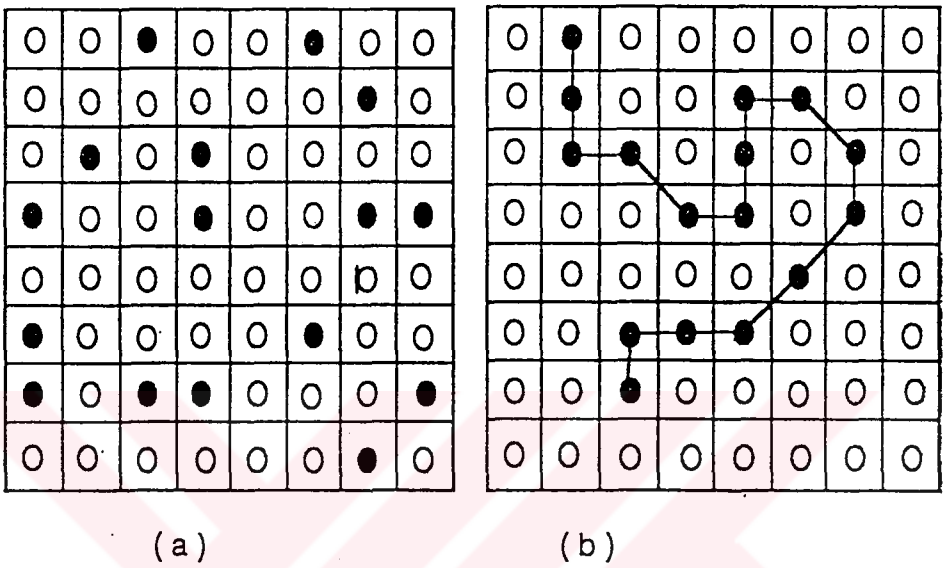

Figure 2.1 **(a)** Representation of two dimensional Flory-Huggins lattice containing solvent molecules (o) and a low-molecular-weight solute (•).
(b) Lattice model for a polymer chain in solution. Symbols represent solvent molecules (o) and polymer-chain segments (•).

2.2 Thermodynamics of Polymer Solutions

2.2.1 Entropy of Mixing in Polymer Solutions

The polymer solutions invariably exhibit large deviations from Raoult's Law except at extreme dilution[19]. Deviation from ideality may arise mainly from non-athermal mixing conditions ($\Delta H_m \neq 0$) as well as the large differences in molecular size between the components. When one component of the solution is a polymer, the connectivity of chain segments imposes a special restriction on the arrangement of the two components in space. Flory[20,21] and Huggins[22] independently evaluated the number of distinguishable ways in which N_1 solvent molecules with a molar

volume V_1 and N_2 polymer chains with a molar volume V_2 could be placed on a lattice as shown schematically in Figure 2.1b, so that each lattice site is occupied either by a solvent molecule or one of the $x = V_2 / V_1$ segments of a polymer chain. The total number of lattice sites is thus equals to;

$$N_0 = N_1 + xN_2 \tag{2.7}$$

According to the Flory-Huggins (F-H) theory, the individual numbers of possible placements are calculated for each segment of the chain, and by multiplying these numbers together the total number of possible conformations of the polymer molecules in the lattice is (ν) obtained. For instance, let i chains have already been inserted into the lattice, the number of possible conformations for the (i+1)th polymer molecule (ν_{i+1}) is given by;

$$\nu_{i+1} = \left\{\frac{(N_0 - xi)!}{[N_0 - x(i+1)]!}\right\}\left[\frac{z-1}{N_0}\right]^{x-1} \tag{2.8}$$

where z is the coordination number of the lattice or the number of cells that are first neighbour to a given cell. The total number of distinguishable ways of placing the N_2 chains on $N_1 + xN_2$ sites is;

$$\Omega = \frac{1}{N_2!}\prod^{N_2-1}\nu_{i+1} \tag{2.9}$$

The number of ways Ω_2 by which chains can be placed on xN_2 sites is obtained by setting $N_1 = 0$ in Equation (2.9). The configurational entropy of mixing is;

$$\Delta S_m = k \ln \frac{\Omega}{\Omega_2} = -k[N_1 \ln \nu_1 + N_2 \ln \nu_2] \tag{2.10}$$

where ν_1 and ν_2 are the volume fractions of solvent and polymer defined as;

$$\nu_1 = \frac{N_1}{N_1 + xN_2} \quad , \quad \nu_2 = \frac{xN_2}{N_1 + xN_2} \tag{2.11}$$

Equation (2.10) can be simplified by multiplication by N_A and hence,

$$\Delta S_m = -R[n_1 \ln \nu_1 + n_2 \ln \nu_2] \tag{2.12}$$

Equation (2.12) is the expression for the configurational entropy of mixing of an athermal polymer solution and comparison with Equation (2.5) shows that they are similar in form except for the fact that mole fractions occuring in the ideal expression are replaced with volume fractions. This change arises from the differences in size between the components.

2.2.2 Enthalpy and Free Energy of Mixing in Polymer Solutions

In the polymer solutions, there are both segment-solvent and segment-segment interactions within the same chain. The segment-solvent interaction is intermolecular interaction while the second is intramolecular interaction. Thus, three types of contact represented by the self-explanatory symbols [1,1], [1,2], [2,2] and three corresponding kinds of energy, w_{11}, w_{12}, w_{22} need to be considered. Enthalpy change on mixing is assumed to arise from the formation of new solvent-segment contacts on mixing which replace some of the solvent-solvent and segment-segment contacts present in the pure solvent, and the pure polymer components respectively. The change in the internal energy for the formation of an unlike molecular pair (solvent-segment or [1,2]) contacts was given by the mean field expression as[21];

$$\Delta w_{12} = w_{12} - 1/2(w_{11} + w_{22}) \tag{2.13}$$

and the expression for the enthalpy of mixing was then written as[21];

$$\Delta H_m = zN_1\nu_2\Delta w_{12} \tag{2.14}$$

To eliminate z and Δw_{12} a parameter called Flory (or polymer-solvent) interaction parameter (χ_1) was introduced;

$$\chi_1 = \frac{z\Delta w_{12}}{kT} \tag{2.15}$$

The expression for the enthalpy of mixing was then rewritten by combining Equations (2.14) and (2.15) as[21];

$$\Delta H_m = kT\chi_1 N_1 \nu_2 \tag{2.16}$$

The quantity $kT\chi_1$ represents merely the difference in energy of a solvent molecule immersed in the pure polymer $(\nu_2 \cong 1)$ compared with one surrounded by molecules of its own kind, i.e., in the pure solvent.

The free energy of mixing can simply be obtained by combining Equations (2.12) and (2.16) as;

$$\Delta G_m = RT\left[n_1 \ln \nu_1 + n_2 \ln \nu_2 + n_1 \chi_1 \nu_2\right] \tag{2.17}$$

2.3 Swelling of Polymer Networks

The polymer networks are held together chemically and/or physically by secondary forces (van der Waals, hydrogen bonding, etc.) among some segments of the polymer chains. The number of chains meeting at each junction is called the functionality (Φ). The networks have a structure of the type sketched in Figure 2.2 where clusters of sticky ends form the nodes of the network[23]. Three types of chains can be distinguished in the figure; (i) chains which connect different nodes (network chains); (ii) chains which close into a loop (cycles); and (iii) dangling chains.

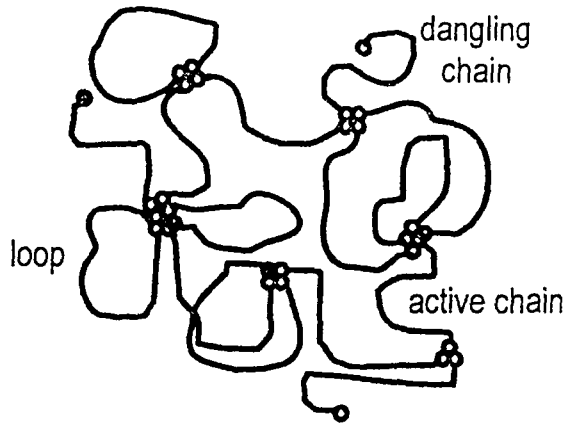

Figure 2.2 Schematic representation of a network formed by chains with 'sticky' ends.

A chain connected to a junction of the network at only one end is called a dangling chain, and one having both its ends attached to the same junctions is called a loop. The network with no dangling chains or loops and in which all junctions have a functionality greater than two is called a perfect network can never be obtained in reality[24].

Swelling is one of the characteristic features of polymer networks. The ability to absorbe good solvents arises from the spontaneity of the mixing processes (Equation 2.12), while their resistance to dissolution arises from crosslinks between the network chains. As the network is swollen by absorption of solvent, the chains between network junctions are required to assume elongated configurations. As a consequence, a force akin to the elastic retractive force develops. As swelling proceeds, this force increases and the diluting force decreases. Ultimately, a state of equilibrium swelling is reached in which these two forces are in balance. A close analogy exists between swelling equilibrium and osmotic equilibrium. The elastic reaction of the network structure may be interpreted as a pressure acting on the solution, or swollen gel. In the equilibrium state this pressure is sufficient to increase the chemical potential of the solvent in the solution, so that it equals that of the excess solvent surrounding the swollen gel. Swelling of polymer networks is a thermodynamic phenomenon, and it gives a measure of the amount of solvent sorbed by the polymer under equilibrium conditions. In case of swelling in solvent mixtures, it additionally gives a measure of the distribution of solvent components between the

gel and solution phases. At constant temperature, the equilibrium swelling in solvent mixtures can be classified into three general types:

Type 1: The solvent composition inside the polymer network (gel) is proportional to the external solvent composition. Such a case can be considered as an ideal system where the sorption of solvent in polymers is comparable to the Henry's law. For ideal systems, the sorption isotherm is assumed to be linear, i.e., the solvent concentration inside the gel is proportional to that outside.

Type 2: If the attractions between solvent molecules are stronger than the attractions between the solvent molecule and the polymer, then adding one solvent to the other actually decreases the chance of the solvent molecules partition within the polymer network, and lowers the total swelling. Because the total swelling is lowered, this behavior is termed negative deviation.

Type 3: The total swelling is above the swelling of either pure constituents. In this case, unlike solvent molecules may interact with one another less than the solvent molecule and the polymer do. Because the total swelling is increased relative to the ideal behavior, this behavior is termed positive definition [25].

2.4 Theory of Swelling

The Flory-Rehner phenomenological theory has been most widely used to describe the change in the Gibbs free energy (ΔG) during the swelling process[21,26]. This theory assumes that ΔG of swelling equals to the sum of the individual free energy terms, i.e., the changes in the free energy of mixing (ΔG_m), in the free energy of elastic deformation (ΔG_{el}), and in case of ionic network, in the free energy of electrostatic interactions (ΔG_i);

$$\Delta G = \Delta G_m + \Delta G_{el} + \Delta G_i \qquad (2.18)$$

2.4.1 Swelling Thermodynamics of Nonionic Networks

If the network is made up only of neutral monomers, ΔG_m and ΔG_{el} sum up to generate the total Gibbs free energy of the system, i.e.,

$$\Delta G = \Delta G_m + \Delta G_{el} \tag{2.18a}$$

The derivation of ΔG_m within the framework of FH theory was already given in Section 2.2.2. For multicomponent systems, Equation (2.27) can be written as;

$$\Delta G_m = RT\left(\sum_i n_i \ln \nu_i + \sum_{i<j} n_i \nu_j \chi_{ij}\right) \tag{2.19}$$

where n_i is the moles of the species i, ν_i is its volume fraction, χ_{ij} is the interaction parameter between the species i and j.

For the free energy of elastic deformation (ΔG_{el}) several theories are available[21,27,28]. The simplest affine network model in which the junction points are assumed to be embedded in the network is widely used to describe qualitatively the elasticity of networks. As a result of this assumption, components of each chain vector transforms linearly with macroscopic deformation. The change in the free energy of elastic deformation of the affine network is given by[29];

$$\Delta G_{el} = (1/2)(RT/NV_1)(\alpha_X^2 + \alpha_Y^2 + \alpha_Z^2 - 3 - \ln(\alpha_X \alpha_Y \alpha_Z)) \tag{2.20}$$

where N is the average number of segments in the network chains, and V_1 is the molar volume of solvent and,

$$\alpha_X^2 = \frac{\langle x^2 \rangle}{\langle x^2 \rangle_0}, \qquad \alpha_Y^2 = \frac{\langle y^2 \rangle}{\langle y^2 \rangle_0}, \qquad \alpha_Z^2 = \frac{\langle z^2 \rangle}{\langle z^2 \rangle_0}, \tag{2.21}$$

where x, y and z are the components of chain end-to-end distance, the subscript o indicates relaxed state. If α represents the linear deformation factor, then by the condition of isotropy $\alpha = \alpha_X = \alpha_Y = \alpha_Z$. The linear deformation factor α is related to equilibrium swelling ratio by the following equation;

$$\alpha = \left(\frac{v_2^0}{v_2} \right)^{1/3} \tag{2.22}$$

where v_2 and v_2^0 are the volume fractions of the polymer network at equilibrium degree of swelling and after the gel preparation, respectively. If the polymer network is prepared by crosslinking of polymer chains without solvent, as was considered in Flory's original theory[21], v_2^0 must be equal to 1. Equation (2.20) can now be given in terms of α as;

$$\Delta G_{el} = (3/2)(RT/NV_1)(\alpha^2 - 1 - \ln\alpha) \tag{2.23}$$

Substituting Equation (2.22) into Equation (2.23) leads to;

$$\Delta G_{el} = (3/2)(RT/NV_1)\left((v_2^0/v_2)^{2/3} - 1 - \ln(v_2^0/v_2)^{1/3}\right) \tag{2.24}$$

Substitution of Equations (2.19) and (2.24) into Equation (1.18a) gives the free energy equation of swelling for non-ionic (uncharged) networks;

$$\Delta G = RT\left(\sum_i n_i \ln v_i + \sum_{i<j} n_i v_j \chi_{ij} + \frac{3}{2}\frac{1}{NV_1}\left((v_2^0/v_2)^{2/3} - 1 - \ln(v_2^0/v_2)^{1/3}\right)\right) \tag{2.25}$$

2.4.2 Swelling Thermodynamics of Ionic Networks

If the polymer chains making up the network contain ionizable groups, the electrostatic force due to fixed charges should be taken into account. The existence of fixed ions on the network chains results in non-equal distribution of mobile

counterions between the inside and outside the gel. Thus, the change in the free energy of electrostatic interactions (ΔG_i) may be written as follows[21,30];

$$\Delta G_i = RTf \frac{v_2}{v_1} n_1 \ln(f v_2) \tag{2.26}$$

where f is the effective charge density of the network, i.e., the fraction of segments bearing ionic groups.

Substitution of Equations (2.19), (2.24) and (2.26) into Equation (2.18) gives the free energy equation of swelling for ionic networks;

$$\Delta G = RT\left(\sum_i n_i \ln v_i + \sum_{i<j} n_i v_j \chi_{ij} + \frac{3}{2}\frac{1}{NV_1}\left((v_2^0/v_2)^{2/3} - 1 - \ln(v_2^0/v_2)^{1/3}\right) + f\frac{v_2}{v_1} n_1 \ln(f v_2)\right) \tag{2.27}$$

The exchange of ions and solvent between a swollen ionic network and the surrounding electrolyte is represented in Figure 2.3, where the fixed ion is taken to be a cation. It is appearent that the equilibrium between the swollen ionic gel and its surrounding closely resembles Donnan membrane equilibria. The polymer acts as its own membrane preventing the charged substituents, which are distributed essentially at random through the gel from diffusing into the outer solution. The swelling force resulting from the presence of these fixed charges may be identified with the swelling pressure or osmotic pressure, across the semipermeable membrane in a typical Donnan equilibrium. Because of the attracting power of the fixed charges, the concentration of mobile ions will always be greater in the gel than outside. Consequently, the osmotic pressure of the solution inside will exceed that of the external solution. The swelling force may be equated to this difference in osmotic pressures for the two solutions.

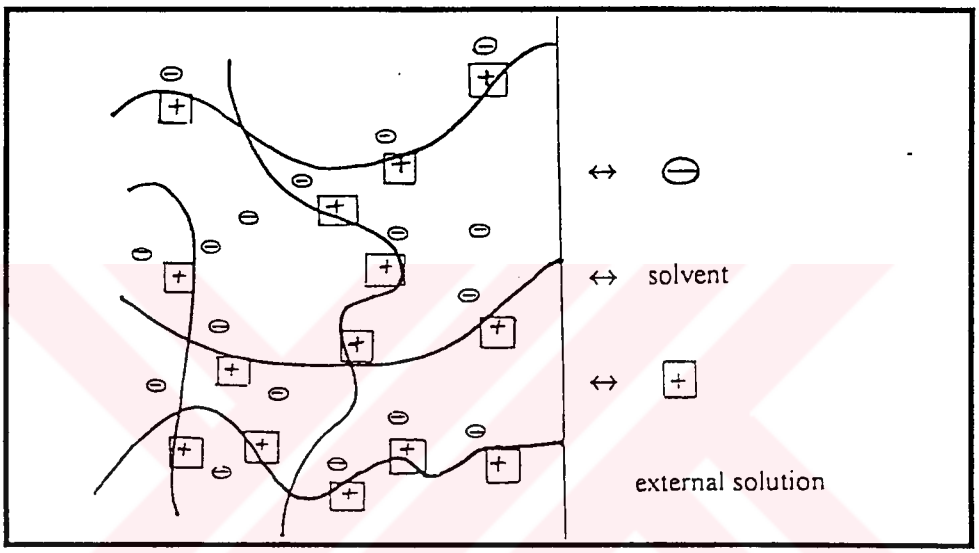

Figure 2.3 Diagram of swollen ionic gel in equilibrium with electrolyte solution. Fixed charges are represented by +[1]

3. PHASE EQUILIBRIA IN POLYMER SYSTEMS

The most basic problem in the phase equilibrium of polymer solutions is to find analytical expression for ΔG which allow quantitative prediction of the phase relationships of various polymer solutions. However, none of the available mathematical expressions for ΔG are yet fully adequate for predicting phase equilibrium behavior of polymer solutions, i.e., a binary system made up of a monodisperse (homo) polymer and a solvent and quasi-binary solutions consist of two or more homologous monodisperse polymers and a single solvent. This situation results from two major reasons; the lack of theories which can be easily extended to multicomponent polymer-solvent mixtures, and their inherent mathematical difficulties.

3.1 Polymer-Solvent Miscibility

The mutual solubility of a polymer-solvent system can be best understood by referring to the free energy of the system as a function of composition. A schematic representation of the free energy of mixing is shown in Figure 3.1a. The curve for T_5 is concave upward and has no inflection point. If the free energy-composition curve has a shape which allows a tangent to touch it at two points, phase separation will occur. If two separate phases are present in the system, they will always correspond to a higher free energy and hence, are unstable with respect to the homogeneous phase. Total miscibility occurs when the Gibbs free energy of mixing is less than the Gibbs free energies of the components. For total missibility, it is necessary that;

$$\Delta G_m \langle 0 \qquad (3.1)$$

The phase equilibrium is strongly affected by solution temperature. Figure 3.1 shows the transition from a system miscible in all proportions at a temperature T_5 through the critical temperature, to partially miscible systems at temperatures T_3 to T_1. At each lower temperature, mixtures of the polymer and solvent over a certain composition range will separate into two phases. The temperature-concentration phase diagram (Figure 3.1b) consists of a boundary curve distinguishing the homogeneous from the heterogeneous region. The two phases represented by α and β share a common tangent of the ΔG_m curve. A homogeneous phase is stable if its composition is either smaller than α or larger than β. At compositions intermediate between α and β, any single phase is thermodynamically unstable. As the free energy curve passes from one minimum to another, there are two inflection points at which the second derivative of ΔG_m with respect to the mole fraction of polymer is zero.

$$\left(\frac{\partial^2 \Delta G_m}{\partial x_2^{\,2}}\right)_{P,T} \rangle 0 \qquad (3.2)$$

Mixtures falling inside this so-called binodial curve which is the loci of points that satisfy the conditions for thermodynamic equilibrium of a binary mixture. The maximum in the binodal curve is a critical point for the binary system; the composition of the coexisting phases merge at this point, and at temperatures above the critical temperature (T_C) the system is homogeneous for all compositions[31,32].

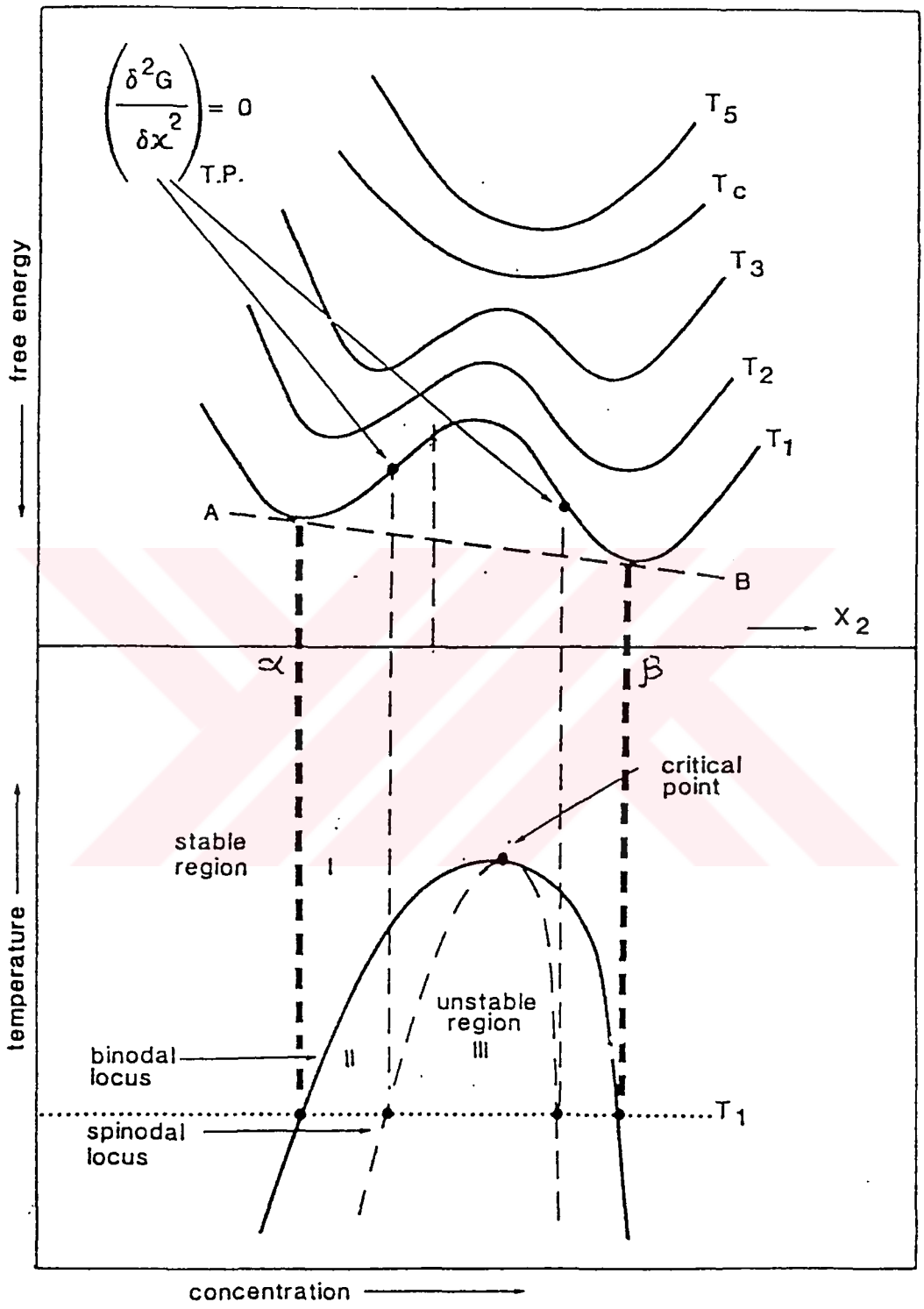

Figure 3.1 (a) Schematic diagram of the Gibbs free energy of mixing (ΔG_m) as a function of the mole fraction of polymer.
(b) Temperature-concentration diagram of binary mixtures.

3.2 Binary Polymer-Solvent Systems

If the polymer consists of a sufficiently narrow range of molecular species, the mixtures of solvent and polymer may be treated as binary solution system. The condition for equilibrium between two phases in a binary system is that the chemical potential of each component be equal in each phase. The partial molar Gibbs free energy of mixing ($\Delta\overline{G}_i$) which is called excess chemical potential ($\Delta\mu_i$) is defined as;

$$\Delta\overline{G}_i = \Delta\mu_i = \left(\frac{\partial \Delta G_m}{\partial n_i}\right)_{T,P,n_j} \tag{3.3}$$

The free energy relation of mixing of a homogeneous chain polymer of uniform molecular weight in a single uniform solvent was calculated by Flory and Huggins and was explained in Section 2.2.2. The situation is however more complicated in the case of polymers consisting of a heterogeneous distribution of chain lenghts[33]. By making the similar assumptions as those of Huggins, and differentiating the Equation (2.19) with respect to the number moles of the solvent molecules (n_1) the partial molal free energy of mixing of solvent with a polydisperse polymer was found to be[33];

$$\Delta\mu_1 = RT\left[\ln(1-\nu_2)+\nu_2\left(1-\frac{1}{\overline{X}_n}\right)+\chi\nu_2^{\,2}\right] \tag{3.4}$$

where $\overline{X}_n$ is the number average degree of polymerization which is defined as;

$$\overline{X}_n = \frac{\sum_i n_i X_i}{\sum_i n_i} \tag{3.5}$$

where n_i and X_i are the moles and the degree of polymerization of polymer chains i, respectively. When the solution under consideration separates into two equilibrium phases, the following phase equilibrium relations must hold;

$$\Delta\mu_1' = \Delta\mu_1'' \qquad \text{(solvent)} \qquad (3.6)$$

$$\Delta\mu_2' = \Delta\mu_2'' \qquad \text{(polymer)} \qquad (3.7)$$

where single and double primes are adopted as the designation for the dilute and concentrated phases. Before proceeding from these conditions to the deduction of the concentrations of the two phases in equilibrium, it is instructive to examine the requirements for the occurrence of incomplete miscibility. Fullfilment of the former of the condition (3.6) requires that there must be two concentrations at which the chemical potential $\Delta\mu_1$ has the same value, and this requires that $\Delta\mu_1$ pass through a minimum and then a maximum as v_2 is increased from zero to unity (Figure 3.2). Similarly, in order to comply with the condition (3.7), $\Delta\mu_2$ must exhibit a maximum and a minimum. Since $\Delta\mu_1$ and $\Delta\mu_2$ are derived by differentiating the same free energy function, Equation (2.19), it is easy to show that the one must pass through a maximum where the other is at its minimum, hence it will suffice to consider either chemical potential alone. Confining attention to $\Delta\mu_1$, the inflection point characterized by the condition of zero curvature $(\partial^2\Delta\mu_1/\partial v_2^{\,2})_{T,P} = 0$, must necessarily occur between the minimum and the maximum in the curve.

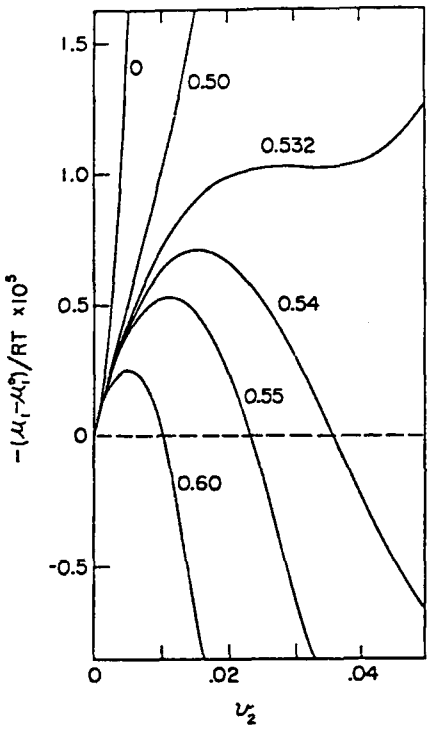

Figure 3.2 The chemical potential of the solvent in a binary solution containing polymer at low concentrations. The values of χ indicated with each curve [20].

At both the maximum and the minimum $(\partial \Delta\mu_1/\partial v_2)_{T,P} = 0$. Manifestation of these characteristics in the function representing $\Delta\mu_1$ constitutes the necessary and sufficient condition for incomplete miscibility. If the curve representing $\Delta\mu_1$ as a function of composition decreases monotonically with v_2, total miscibility is assured. In passing to progressively poorer solvents, eventually a minimum and a maximum will appear in the curve; their appearance signifies incomplete miscibility. Ordinarily a poor solvent for a given polymer becomes poorer with lowering of the temperature; hence an initially totally miscible system at higher temperatures may be transformed to one of limited miscibility by lowering the temperature. Thus, the critical solution temperature (T_C) is an important quantity, and at this temperature incipient phase separation will be encountered. Hence the conditions for incipient phase separation are;

$$\left(\frac{\partial \Delta\mu_1}{\partial v_2}\right)_{T,P} = 0 \qquad \text{and} \qquad \left(\frac{\partial^2 \Delta\mu_1}{\partial {v_2}^2}\right)_{T,P} = 0 \tag{3.8}$$

Application of the critical conditions to Equation (3.4) leads to the first derivative of that equation;

$$\frac{1}{1-v_{2C}} - \left(1 - \frac{1}{\overline{\overline{X}}_n}\right) - 2\chi_C v_{2C} = 0 \tag{3.9}$$

while the second derivative is;

$$-\frac{1}{(1-v_{2C})^2} + 2\chi_C = 0 \tag{3.10}$$

where the subscript c denotes the critical conditions. The critical composition at which phase separation is first detected is then;

$$v_{2C} = \frac{1}{1+\sqrt{\overline{\overline{X}}_n}} \tag{3.11}$$

$$\chi_C = \frac{1}{2}\left(1 + \frac{1}{\sqrt{\overline{\overline{X}}_n}}\right)^2 \tag{3.12}$$

The critical value of χ approaches a limiting value of 1/2 for infinite molecular weight. The temperature at which phase separation begins is given by;

$$\psi_1\left[1 - \frac{\theta}{T_C}\right] = \frac{1}{2} - \chi_C \tag{3.13}$$

Combination with Equation (3.12) gives;

$$\frac{1}{T_C} = \frac{1}{\theta}\left[1 + \frac{1}{\psi_1}\left(\frac{1}{\sqrt{\bar{X}_n}} + \frac{1}{2\bar{X}_n}\right)\right] \tag{3.14}$$

which predicts a linear relation between $1/T_C$ and $\left(1/\sqrt{\bar{X}_n} + 1/2\bar{X}_n\right)$ and is verified by experimental results[34]. It can be seen from Equation (3.14) that the theta temperature is also the critical miscibility temperature in the limit of infinite molecular weight[21,24].

3.3 Swelling Equilibrium of Polymer Network in a Single Solvent

Dusek, Patterson and Prins[4,35] presented a theoretical analysis of equilibrium swelling of a network in a single solvent in the late 1960s. This study lead to the prediction that a swollen network in equilibrium with pure solvent may undergo a phase transition into two phases with different degrees of swelling.

According to Equation (2.27), the change in the free energy of an ionic polymer network during swelling in a single solvent (i=1 and 2) can be written as:

$$\frac{\Delta G}{RT} = n_1 \ln v_1 + n_2 \ln v_2 + n_1 v_2 \chi + \frac{3}{2}\frac{1}{NV_1}\left[\left(\frac{v_2^0}{v_2}\right)^{2/3} - 1 - \ln\left(\frac{v_2^0}{v_2}\right)^{1/3}\right] + \frac{f}{N}\frac{v_2}{v_1} n_1 \ln\left(\frac{f v_2}{N}\right) \tag{3.15}$$

Differenting Equation (3.15) with respect to the number of moles of solvent (n_1) yield the equation for excess chemical potential of the solvent;

$$\frac{\Delta\mu_1}{RT} = \ln(1 - v_2) + v_2 + \chi v_2^{\,2} + \frac{1}{N}\left(v_2^{1/3} v_2^{0\,2/3} - \frac{v_2}{2}\right) - f v_2 \tag{3.16}$$

In the original theory[21], χ was assumed to be a constant for a given polymer-solvent system and temperature. However, χ usually varies with the polymer concentration given by the empirical equation[36];

$$\chi = \chi_1 + \chi_2 v_2 \tag{3.17}$$

where χ_1 and χ_2 are the coefficients. At the critical point, according to Equation (3.8) both the first and second derivatives of the excess chemical potential of solvent, $\Delta\mu_1$ with respect to v_2 equate to zero. Substitution of Equation (3.17) in the expression for the excess chemical potential of solvent (Equation 3.16) and application of the critical conditions to the same equation lead to the first derivative of that equation;

$$\frac{-v_2}{1-v_2} + 2\chi_{1C} v_2 + 3\chi_{2C} {v_2}^2 + \frac{1}{3} N^{-1} {v_2}^{-2/3} v_2^{0/3} - \frac{1}{2} N^{-1} - f = 0 \tag{3.18}$$

while the second derivative is;

$$-\frac{1}{(1-v_2)^2} + 2\chi_{1C} + 6\chi_2 v_{2C} - \frac{2}{9} N^{-1} v_2^{0/3} {v_2}^{-5/3} = 0 \tag{3.19}$$

where the subscript c denotes the critical conditions. The theoretical calculations according to Equations (3.16), (3.18) and (3.19) show that when the χ parameter is expressed as a linear function of v_2, the required conditions for the coexistence of two gel phases in equilibrium with pure solvent are;

$$\chi_{1C} = \frac{1}{(1-v_2)^2}\left(\frac{1}{2} - v_2\right) - \frac{8\alpha^2 - 9}{18 N v_2} + \frac{f}{v_2} \tag{3.20}$$

$$\chi_{2C} = \frac{1}{3(1-v_2)^2} + \frac{10\alpha^2 - 9}{54 N {v_2}^2} - \frac{f}{3{v_2}^2} \tag{3.21}$$

These equations show that concentration dependence of the solvent-network interaction parameter χ may cause discontinuous swelling transition even in non-ionic gels. At the critical point, the coefficients χ_1 and χ_2 reduce to $\chi_{1C} \leq 1/2$ and

$\chi_{2C} \rangle 1/3$ for $v_2 = 0$, indicating that a discontinuous volume phase transition in non-ionic network can be induced if χ strongly depends on concentration[36].

3.4 Swelling Equilibrium of Polymer Networks in Linear Polymer Chains

When the polymer network is immersed in the melt of a linear polymer, according to Equation (2.27), the change in the free energy of this system can be written as sum of three free energy terms;

$$\frac{\Delta G}{RT} = n_2 \ln v_2 + n_3 \ln v_3 + x n_2 v_3 \chi_{23} + \frac{3}{2}\frac{1}{NV_1}\left[\left(\frac{v_2^0}{v_2}\right)^{2/3} - 1 - \ln\left(\frac{v^0}{v_2}\right)^{1/3}\right]$$

$$+ \frac{f}{N}\frac{x n_2}{x n_2 + y n_3}\ln\left(\frac{f v_2}{N}\right) \qquad (3.22)$$

Note that the component 1 (solvent) is absent in the present system. Differentiating Equation (3.22) with respect to the number of moles of linear polymer (n_3) yields the equation for excess chemical potential of the linear polymer which is equal to zero for networks in equilibrium with a polymer melt;

$$\frac{\Delta\mu_3}{yRT} = \frac{1}{y}\ln(1 - v_2) + \frac{v_2}{y} + \chi_{23} v_2^{\,2} + N^{-1} v_2^{0\,2/3} v_2^{\,1/3} - N^{-1}\frac{v_2}{2} - f v_2 = 0 \qquad (3.23)$$

where y is the number of segments in the linear polymer, v_3 is its volume fraction in the gel phase, and χ_{23} is the interaction parameter between the network and the linear polymer. At the critical point, first and second derivatives of Equation (3.23) with respect to v_2 equate to zero;

$$\left(\frac{\partial \Delta\mu_3 / yRT}{\partial v_2}\right)_{T,P} = 0 \quad \text{and} \quad \left(\frac{\partial^2 \Delta\mu_3 / yRT}{\partial v_2^{\,2}}\right)_{T,P} = 0 \qquad (3.24)$$

Application of these critical conditions to Equation (3.23) leads to the first derivative of that equation;

$$\frac{-\nu_2}{y(1-\nu_2)} + 2\chi_{23C}\nu_2 + \frac{1}{3}N_C^{-1}\nu_2^{0\frac{2}{3}}\nu_2^{-\frac{2}{3}} - \frac{1}{2}N_C^{-1} - f = 0 \qquad (3.25)$$

while the second derivative is;

$$-\frac{1}{y(1-\nu_2)^2} + 2\chi_{23C} - \frac{2}{9}N_C^{-1}\nu_2^{0\frac{2}{3}}\nu_2^{-\frac{5}{3}} = 0 \qquad (3.26)$$

Simultaneous solution of Equations (3.23), (3.25) and (3.26) shows that the critical conditions for the coexistence of two gel phases in the state of equilibrium swelling of the polymer network immersed in the melt of the linear polymer are;

$$\chi_{23C} = \frac{1}{y(1-\nu_2)^2}\left[\frac{1}{2} + \frac{2\nu_2\alpha^2}{9-10\alpha^2}\right] - \frac{2f\alpha^2}{\nu_2(9-10\alpha^2)} \qquad (3.27)$$

$$N_C^{-1} = \frac{18}{9-10\alpha^2}\left[\frac{\nu_2^{\,2}}{y(1-\nu_2)^2} - f\right] \qquad (3.28)$$

It is seen that the critical value of χ_{23} parameter for non-ionic networks equals to $1/2y$ for $\nu_2 = 0$. Thus, χ_{23C} decreases as the molecular weight of polymer chains increases.

3.5 Ternary Polymer Network-Solvent-Linear Polymer Systems

The theoretical investigation of swelling of polymer networks in a solution of a linear polymer was first described by Boyer[37]. Although first theoretical studies on this system assumed that the linear polymers can not enter the gel phase[37], recent experimental results indicate that the linear polymers can penetrate into the network,

depending on the thermodynamic parameters of the system, leading to the contraction of the gel. Furthermore, theoretical calculations using the classical F-H theory predicted the possibility of a first-order (discontinuous) phase transition in such systems[8,38].

The state of equilibrium swelling of a polymer network immersed in a polymer solution is obtained when the solvent and the linear polymer inside the network are in thermodynamic equilibrium with those outside. This equilibrium state is described by the equality of the chemical potential (μ) of these components in both phases:

$$\Delta\mu_1^{gel} - \Delta\mu_1^{sol} = 0 \tag{3.29}$$

$$\Delta\mu_3^{gel} - \Delta\mu_3^{sol} = 0 \tag{3.30}$$

Differentiating Equation (2.27) with respect to the number of moles of the solvent (n_1) and the linear polymer (n_3) yield the following set of equations for the excess chemical potentials of the solvent and the polymer in both gel ($\Delta\mu_i^{gel}$) and solution phases ($\Delta\mu_i^{sol}$)[39];

$$\frac{\Delta\mu_1^{gel}}{RT} = \ln v_1 + (1-v_1) - v_3/y + (\chi_{12}v_2 + \chi_{13}v_3)(1-v_1) - \chi_{23}v_2v_3 + N^{-1}\left(v_2^{1/3}v_2^{o\,2/3} - v_2/2\right) - fv_2 \tag{3.31}$$

$$\frac{\Delta\mu_1^{sol}}{RT} = \ln(1-\phi) + \phi(1-1/y) + \chi_{13}\phi^2 \tag{3.32}$$

$$\frac{\Delta\mu_3^{gel}}{yRT} = (1/y)\ln v_3 + (1/y)(1-v_3) - v_1 + (\chi_{13}v_1 + \chi_{23}v_2)(1-v_3) - \chi_{12}v_1v_2 + N^{-1}\left(v_2^{1/3}v_2^{o\,2/3} - v_2/2\right) - v_2 f \tag{3.33}$$

$$\frac{\Delta\mu_3^{sol}}{yRT} = (1/y)\ln\phi - (1-\phi) + (1/y)(1-\phi) + \chi_{13}(1-\phi)^2 \tag{3.34}$$

where ϕ is volume fraction of the linear polymer in the solution phase, χ_{12} and χ_{13} are the solvent-network, and solvent- linear polymer interaction parameters. In terms of the osmotic pressure (π), Equation (3.29) can also be written as;

$$\pi = -\frac{\left(\mu_1^{gel} - \mu_1^{sol}\right)}{V_1} = 0 \tag{3.35}$$

Osmotic pressure of a gel determines whether the gel tends to expand or to shrink. When nonzero, π provides a driving force for the gel volume change. The solvent moves into or out of the gel until $\pi = 0$; i.e., until the forces acting on the gel are balanced.

Substitution of Equations (3.31)-(3.34) into Equations (3.29) and (3.30) yields the following two equations describing the thermodynamic equilibrium condition of an ionic gel immersed in a polymer solution;

$$\ln\left(\frac{1-\nu_2-\nu_3}{1-\phi}\right)+(\nu_2+\nu_3-\phi)-(\nu_3-\phi)/y+\chi_{12}\nu_2{}^2+\chi_{13}\left(\nu_3{}^2-\phi^2\right)$$
$$+(\chi_{12}+\chi_{13}-\chi_{23})\nu_2\nu_3+N^{-1}\left(\nu_2{}^{1/3}\nu_2{}^{0\,2/3}-\nu_2/2\right)-f\nu_2=0 \tag{3.36}$$

$$-\ln\left(\frac{1-\nu_2-\nu_3}{1-\phi}\right)+(1/y)\ln(\nu_3/\phi)-2\chi_{13}(\nu_3-\phi)+(\chi_{23}-\chi_{12}-\chi_{13})\nu_2=0 \tag{3.37}$$

Equations (3.36) and (3.37) predict the equilibrium volume fraction of the polymer network in the gel (ν_2) and the concentration of the linear polymer molecules penetrating into the gel phase (ν_3).

Note that the network charge density f in the above equations is not constant and it decreases as the linear polymer concentration increases. It was shown that f depends on ϕ by [10];

T.C. YÜKSEKÖĞRETİM KURULU DOKÜMANTASYON MERKEZİ

$$f = f_0 - A\phi \tag{3.38}$$

where A is the fraction of counterions forming ion pairs in polymer melt and f_0 is the charge density.

3.6 Phase Separation Phenomena in Gels and Gel Collapse

As pointed out before, phase separation phenomena in polymer solutions are brought about by variations in temperature, pressure, ionic concentration of the network, pH and solvent activity. The first and second derivatives of the chemical potential of solvent with respect to ν_2 equate to zero at the critical point for a polymer-solvent systems. A network-solvent system may also exhibit phase separation where three phases of different concentrations may exist in equilibrium: One of the phases is pure solvent $(\nu_2 = 0)$. The remaining two phases are a less swollen and a highly swollen phase. Such a state is referred to as triphasic equilibrium, described by the equations;

$$\Delta\mu_1(\nu_2') = \Delta\mu_1(\nu_2'') = 0 \tag{3.39}$$

where ν_2' and ν_2'' represent the two coexisting polymer concentrations. This state may be reached for example by varying the temperature. Phase diagram of such a system (Figure 3.3) is constructed by calculating the osmotic pressure for many combinations of volume and either temperature or solvent concentration[1].

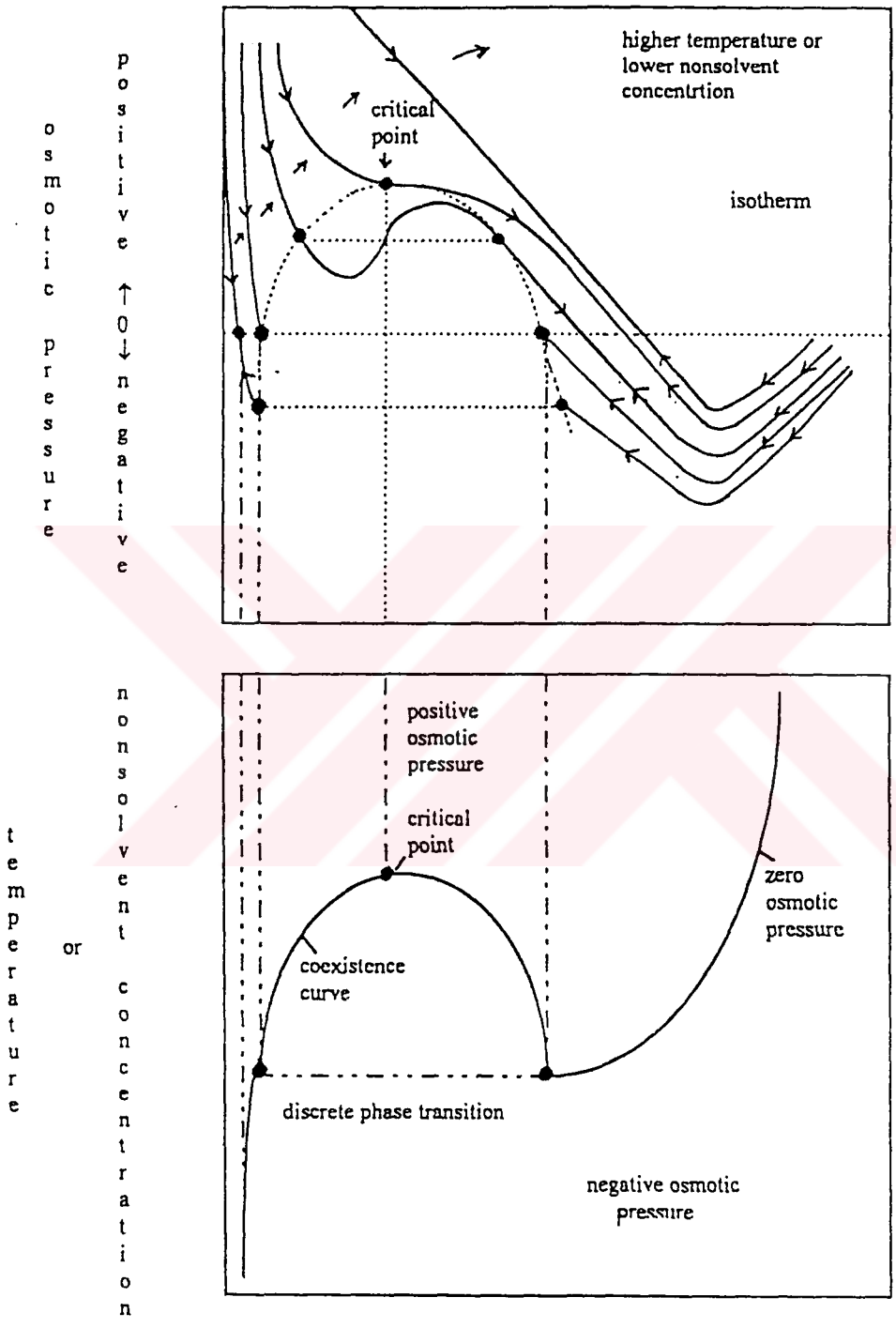

Figure 3.3 Phase Diagram of a Gel[1].

In the lower diagram this information is presented as a series of isotherms, which are curves that specify all possible combinations of pressure and volume at a given temperature. The lower diagram was derived from the upper, but it gives the volume of the gel as a function of temperature or solvent concentration.

The complete phase diagram for the gel has three regions. Below the swelling curve the gel has a negative osmotic pressure and is always unstable; it will expel solvent and shrink until it reaches the zero-pressure swelling curve. Another region represents states with a positive osmotic pressure, which are stable only if there is excess solvent the gel could absorbs in order to expand. Between these realms is the domain of dual stability, where some part of the gel shrinks and another part swells. The boundary of this region is the coexistence curve for the two phases. The difference in volume between the two phases is greatest along the swelling curve, and it decreases steadily at higher temperature. Ultimately the coexistence curve reaches a maximum temperature where the two phases are identical where they cease to exist as distinguishable phases. That is the critical point of the gel[1].

3.7 Molecular Interactions For Volume Phase Transitions of Gels

In this and following section, swelling and collapsing behavior of gels, explained in the previous sections, are given in Tanaka's formalism[2].

The quick and uniform volume phase transition is inversely proportional to the size of gel that is very sensitive to the change in the molecular interactions. Four fundamental molecular interactions that are shown in Figure 3.4 play an essential role in determining the structures and specific functions of macromolecules and their assembles: van der Waals, hydrophobic, electrostatic interactions and hydrogen bonding[2,40,41]. The volume phase transition of gels is a result of a competitive balance between a repulsive force that acts to expand the polymer network and an attractive force that acts to shrink the network. The most effective repulsive force is the electrostatic interaction between the polymer charges of the same kind, which can be imposed upon a gel by introducing ionization into the network. The attractive

interactions can be van der Waals, hydrophobic interaction, ion-ion with opposite kinds, and hydrogen bonding.

3.7.1 Van der Waals Interaction

A partially hdyrolyzed poly(acrylamide) gel undergoes a phase transition in acetone-water mixtures[42]. The main polymer-polymer affinity is due to the van der Waals interaction. Acetone, a nonpolar poor-solvent, had to be added to water in order to increase the attractive interaction between polymers in the networks to induce the transition. The transition is also observed when the temperature was varied while the solvent composition fixed near the transition treshold at room temperature. The gel swells at higher temperatures and shrinks at lower temperatures.

3.7.2 Hydrophobic Interactions

In attempt to find a gel undergoes a volume phase transition in pure water, Hirokawa studied with PNIPA gels that had side groups with more hydrophobicity than that of acrylamide[43]. They observed the collapsing transition at approximately 33.2 °C by increasing temperature. It is interesting to observe that gels swell at lower temperatures and collapse at higher temperatures. This temperature dependence, which is opposite to the transition induced by van der Waals interaction, is due to the hydrophobic interaction of the polymer network and water. At higher temperatures the polymer network shrinks and becomes more ordered, but the water molecules excluded from the polymer network become less ordered.

3.7.3 Electrostatic Interaction

The electrostatic interaction is a long-range order interaction and inversely proportional to the dielectric constant of the medium. In synthetic polymers, either positive or negative charges are introduced on the polymer chains by copolymerization or partial ionization, which give rise to a strong repulsive interaction. Since a free movement of the charges is not allowed because the charges are fixed on the polymer chain, the counter ions have to be localized near the polymer chains so as to keep the electroneutrality. As a result Donnan potential is

created between the inside and outside of the gel, resulting in an increase in the osmotic pressure[2].

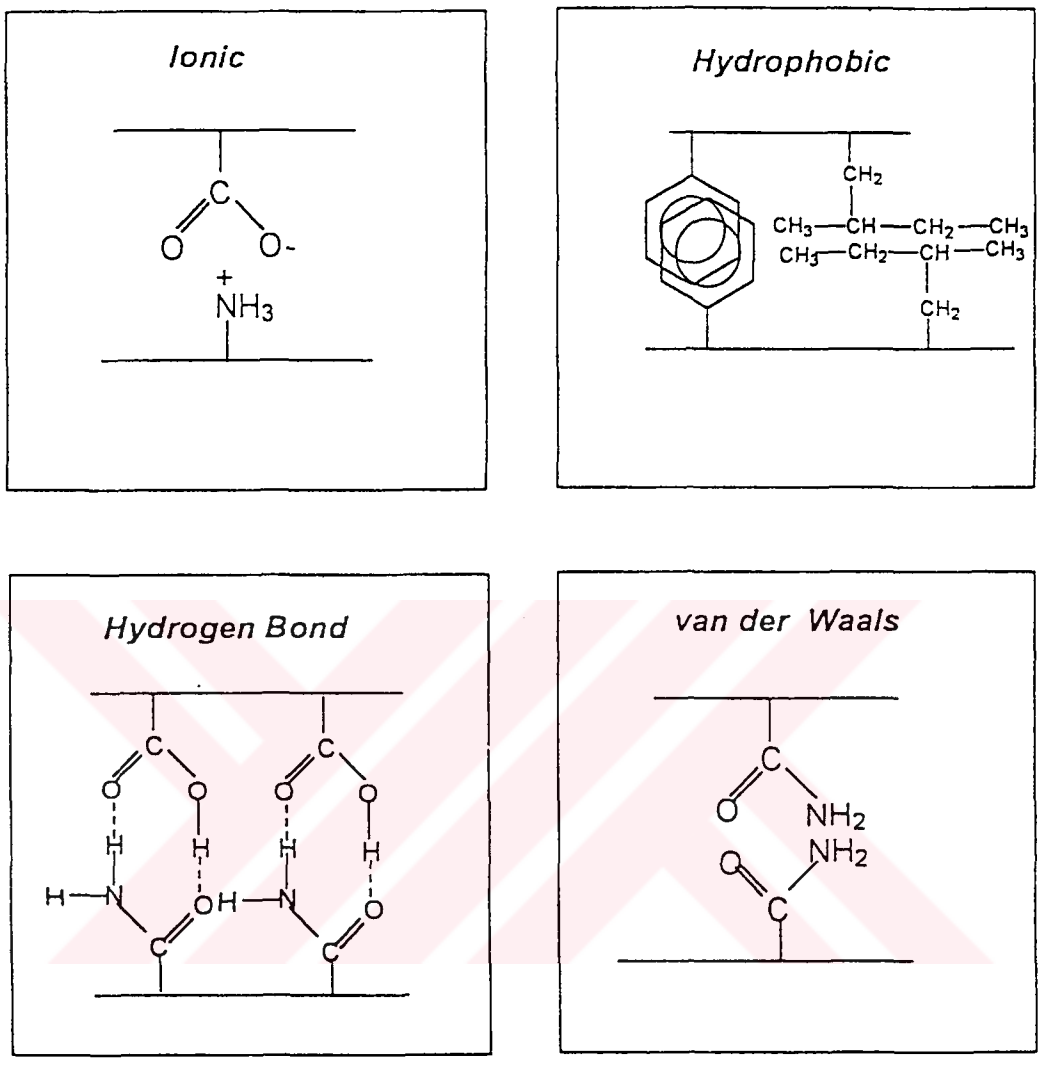

Figure 3.4 Schematic representation showing the four fundamental molecular interactions.

3.7.4 Hydrogen Bonding

A volume phase transition via the hdyrogen bonding interaction was demonstrated with an interpenetrating polymer network (IPN) consisting of two independent networks intermingled with each other. For example, one network is poly(acrylic acid) and the other poly(acrylamide). The gel was originally designed and developed by Okano and his colleagues[44], who found that the gel is shrunken at low temperatures in water, and the volume increased as temperature rose. There was a sharp but continuous volume change at about 30°C. These researchers identified the main interaction to be hydrogen bonding and also pointed out the importance of the so-called "zipper" effect, which describes the cooperative nature of the interaction between two polymers[44]. By slightly ionizing the gel, Ilmain, Tanaka, and Kokufata succeeded in inducing the discontinuous volume transition of the IPN in pure water[45].

3.8 The Physical Nature of The Collapse of a Gel

In order to understand the physical nature of the collapse of a gel, it is necessary to examine all the forces that act to expand or shrink the polymer network. Three such forces have been identified: the rubber elasticity, the polymer-polymer affinity, and the hydrogen-ion pressure. The total pressure acting on the gel is the sum of these three components. This sum is called the osmotic pressure of the gel, because it determines whether the gel tends to take up fluid or to expel it.

For a chain in any given configuration the strength of the rubber elasticity depends on how actively the polymer segments are moving. Because the motions are thermally induced, they are proportional to the absolute temperature; hence the restoring force that tends to extent or contract the chain is also proportional to the temperature. It should be emphasized that the temperature has no effect on the direction of the force, which is determined by whether the chain is stretched or compressed compared with the equilibrium length. The temperature influences only the magnitude or the force.

If the gel is swollen, so that most of the polymer chains are stretched beyond their equilibrium length, the rubber elasticity tends to make the gel contract. Conversely, a collapsed gel tends to expand under the influence of the rubber elasticity. In this way a directed force of tension or compression along a single polymer chain gives rise to a pressure in the gel as a whole. By convention the pressure is positive if it tends to expand the gel, and negative if it tends to make the shrink. Whereas the sign of the pressure depends only on the volume of the gel, its magnitude is determined by the temperature. Raising the temperature strengthens the tendency of a collapsed gel to expand and the tendency of a swollen gel to contract.

The second force acting on the gel, the polymer-polymer affinity, can be traced to an interaction between the polymer strands and the solvent. Such interactions can be either attractive or repulsive, depending mainly on the electrical properties of the molecules. Where the interaction is attractive the polymer can reduce its total energy by surrounding itself with solvent molecules; where the interaction is repulsive the solvent is excluded.

The third and final contribution to the osmotic pressure of the gel, the hydrogen-ion pressure, is associated with the ionization of the polymer network, which releases an abundance of positively charged hydrogen ions (H^+) into the gel fluid. The hydrogen ions can not leave the gel because of the strong electrical attraction between the ions and the negatively charged polymer. Random motions of the hydrogen ions generate a positive pressure. The pressure is directly proportional to the absolute temperature, that is, if the volume of the gel is held constant, raising the temperature increases the hydrogen ion pressure.

4. THEORETICAL WORK

Phenomenological theories of polymeric gels have provided various constitutive equations which describe the swelling behavior of gels fairly well. One of the important aspects of the swelling behavior of PNIPA gels is a reentrant phenomenon where the gels collapse once and reswell as a particular external condition is varied monotonically. In the present study, the swelling behavior of PNIPA gels in polymer solutions was investigated using the classical F-H theory. The system of equations (3.36) and (3.37) was solved simultaneously to calculate the equilibrium volume fraction of crosslinked polymer in the gel (ν_2) as well as the linear polymer partition parameter (ν_3/ϕ) as a function of the volume fraction of the linear polymer in the external solution (ϕ). Simulation technique has been used to investigate the transitions from the swollen to collapsed states and then again to the swollen state and also determine the required condition of reentrant phase transition in PNIPA gels.

For the solution of the thermodynamic equations for the (quasi)ternary system consisting of PNIPA network, linear polymer, and solvent (water), the BASIC program given in the Appendix A was used. The parameters ϕ, y, ν_2^0, N, f_0, and A required for the solution of these equations were evaluated as follows;

1) Concentration (ϕ) and the chain lenght (y) of the linear polymer: ϕ is the volume fraction of the linear polymer in the external solution that is taken as the independent variable in the calculations. The number of segments in the linear polymer is set to 14.7 which corresponds to that of PEG of molecular weight 300 g/mol[46].

2) The network concentration after the gel preparation (ν_2^0) is fixed by the experimental condition and it is taken as 0.06[46].

3) The interaction parameter between PNIPA and water (χ_{12}) was evaluated from the swelling data for non-ionic PNIPA gels swollen in water and it is given as[47];

$$\chi_{12} = 3.415 - \frac{902.2}{T} + 0.518\nu_2 \qquad (4.1)$$

where T is the temperature in Kelvin.

4) The crosslink density (N^{-1}) of the PNIPA gels is fixed at $N = 172$ [47] and the ion pairing coefficient (A) calculated from the swelling data of ionic PNIPA gels in polymer melt[10] was set to 0.68.

5) The temperature of the system (T), the charge density of the network (f_0), the interaction parameters between PNIPA-linear polymer (χ_{23}), and water-linear polymer (χ_{13}) were taken as the independent variables of the present work.

5. RESULTS AND DISCUSSION

The simulated results were evaluated in five categories. In the first three categories, the extent of the interactions between the system components (water, PNIPA network and the linear polymer) is varied and the resulting variations of the swelling behavior of PNIPA gel as well as the partition parameter were investigated. In the last two categories, the effect of the number of segments in the linear polymer (y) and the charge density (f_0) on the swelling behavior of PNIPA gel, in terms of ν_2 were studied.

5.1 Effect of The Linear Polymer-Water Interactions

For the determination of the effect of the linear polymer-water interactions represented by χ_{13} on swelling behavior of non-ionic PNIPA gels in polymer solution, the system of equations (3.36) and (3.37) was solved and the gel composition as well as the partition parameter (ν_3/ϕ) were calculated for different values of χ_{13}. For the calculations, the temperature of the system was taken as 25 °C, χ_{23} parameter was set to zero and χ_{12} parameter was calculated for T= 298 K by using Equation (4.1). The gel composition is represented by ν_i, where the subscript i=1, 2, and 3 denotes the volume fractions of water, PNIPA network, and the linear polymer, respectively.

In Figure 5.1, the PNIPA gel composition (ν_i) for various values of χ_{13} was plotted as a function the volume fraction of the linear polymer in the external solution which were varied between 0 and 1. ϕ increases from 0 to 1 as one move along the composition curve from $\nu_1 - \nu_2$ to $\nu_2 - \nu_3$ sides of the triangle. The $\nu_1 - \nu_2$ side of the triangle corresponds to mixtures of water and PNIPA network, while the $\nu_2 - \nu_3$

side corresponds to mixtures of PNIPA network and the linear polymer. For non-ionic gels and for certain values of ϕ, Equations (3.36) and (3.37) were satisfied by three values of both ν_2 and ν_3, indicating the coexistence of two gel phases with different conformations and appearance of van der Waals loop in the swelling curves. In these cases, the composition of the gels in coexisting phases was calculated by equating chemical potentials of the network chains in both gel phases.

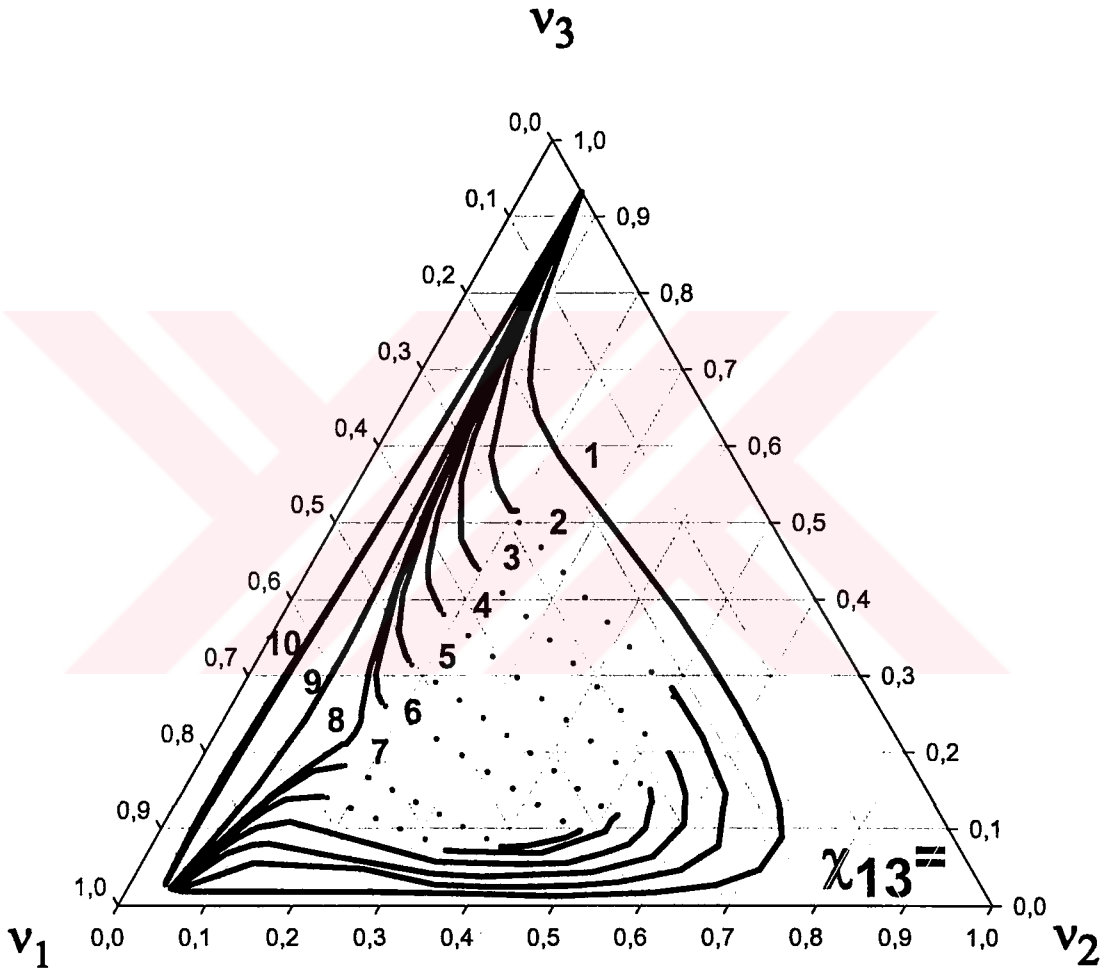

Figure 5.1 Variation of non-ionic PNIPA gel composition with different values of χ_{13}. The dotted lines represent the phase transition regions. T=298 K, $\chi_{23} = 0$ and χ_{13} = - 0.15 (1), -0.05 (2), 0 (3), 0.03 (4), 0.05 (5), 0.06 (6), 0.063 (7), 0.10 (8), 0.45 (9), and 0.60 (10)

In Figure 5.2, for different values of the χ_{13} parameter, the equilibrium volume fraction of crosslinked polymer in the gel was plotted as a function of the linear polymer concentration in the external solution. The curves in the figure indicate that the swelling behavior of PNIPA gels in polymer solution changes drastically depending on a slight change in the values of χ_{13}. Simulated results in Figure 5.2 was discussed in two parts to determine the effect of linear polymer-water interactions (χ_{13}) on the reentrant phase transition behavior of PNIPA gels;

1) Large values of χ_{13}:

For large values of χ_{13} (Curves 13-17 in Figure 5.2), the quality of the solvent (water) for the linear polymer becomes worse, so that repulsive interactions occur between the linear polymer and water. As shown in Figure 5.1, ν_2 does not change much with the linear polymer concentration in the solution (ϕ), while ν_3 monotonically increases with increasing ϕ form 0 to 1. The repulsive interactions between the linear polymer and water ($\chi_{13}>>0$) compared to the attractive interactions between the segments of the linear polymer and PNIPA ($\chi_{23}=0$) facilitate the penetration of linear chains into PNIPA gel. Thus, the higher the linear polymer concentration in the external solution, the greater its penetration into the gel. Figure 5.2 shows that for $0.068 > \chi_{13} > 0.45$, the gel volume remains in the swollen state over the entire range of ϕ, but the solution inside the gel is enriched by the linear polymer as the linear polymer concentration in the solution is increased.

In Figure 5.3, for different values of χ_{13} parameter, the linear polymer partition parameter (ν_3/ϕ) was plotted as a function of the linear polymer concentration in the external solution. ν_3/ϕ represents the ratio of the volume fraction of the linear polymer in the gel phase (ν_3) to that in the solution phase (ϕ); thus, $\nu_3/\phi = 1$ means that the linear polymer concentration inside the gel is equal to that in the solution whereas $\nu_3/\phi = 0$ means that the gel excludes all the linear polymer molecules. As seen in Figure 5.3, the linear polymer concentration inside the gel is always smaller than that in the solution, i.e., $\nu_3/\phi < 1$ due to the reduction in the number of

arrangements available to the linear polymer chains penetrating into the gel. For large values of χ_{13}, the partition parameter reaches values close to 1 over all ϕ (Curves 9-11 in Figure 5.3). As a result, the concentration difference of the linear polymer between the outside and inside the gel phase keeps the gel volume almost constant in polymer solutions.

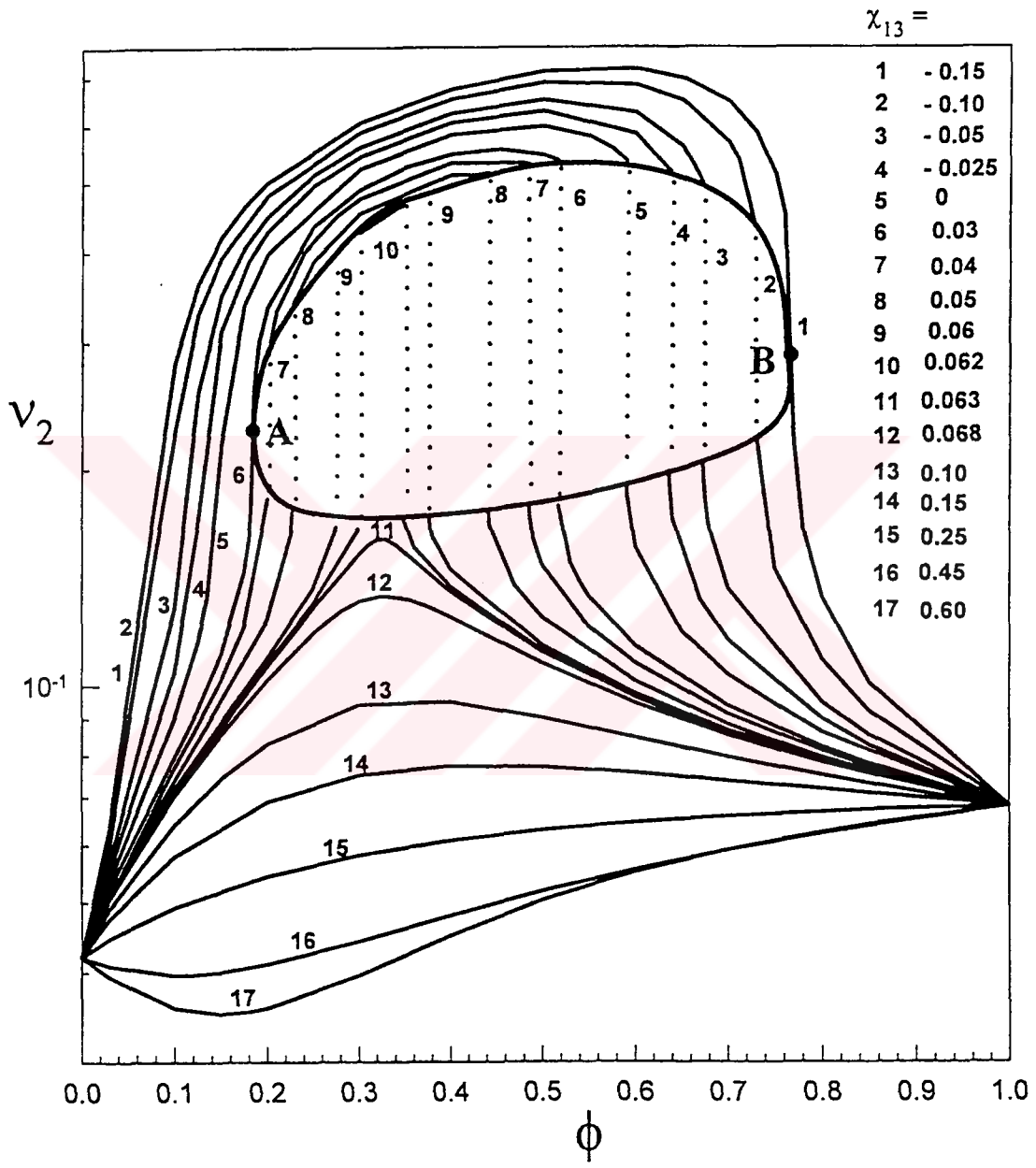

Figure 5.2 The volume fraction of crosslinked polymer in the gel ν_2 shown as a function of the polymer concentration ϕ in the external solution. T = 298 K, $\chi_{23} = 0$ and χ_{13} parameter values are indicated in the figure.

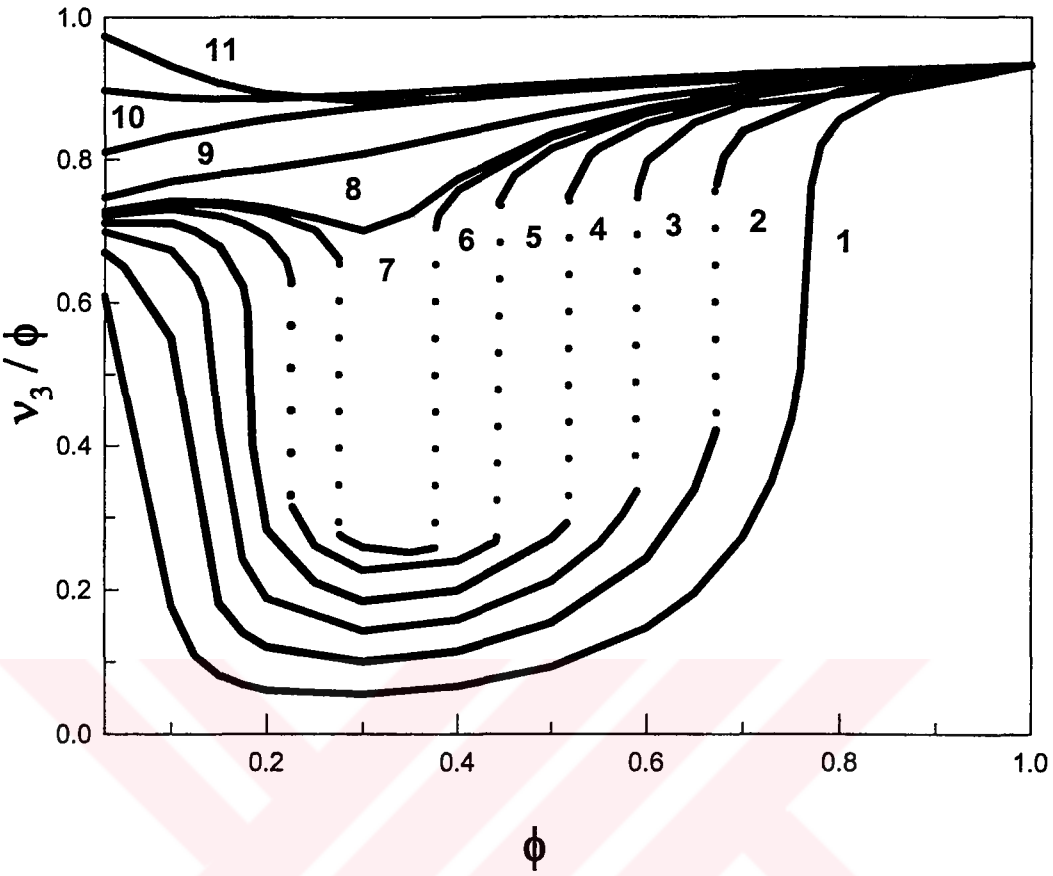

Figure 5.3. The polymer partition parameter ν_3/ϕ shown as a function of the polymer concentration ϕ in the external solution. T = 298 K, χ_{23} = 0, χ_{13} = - 0.15 (1), -0.05 (2), 0 (3), 0.03 (4), 0.05 (5), 0.06 (6), 0.063 (7), 0.10 (8), 0.25 (9), 0.45 (10), and 0.60 (11)

ii) Small or negative values of χ_{13}:

Attractive interactions occur between the linear polymer and water at small or negative values of χ_{13}. The curves 1-10 in Figure 5.2 show that for small or negative values of χ_{13}, the gel exhibits reentrant conformational transitions. At low concentrations of the linear polymer, the equilibrium volume fraction of crosslinked polymer ν_2 rapidly increases while the linear polymer partition parameter (ν_3/ϕ) is a decreasing function of ϕ. Only a small fraction of the linear polymer can penetrate into the hydrogel network while the linear polymer concentration in the solution increases. Hence, the gel starts to deswell. On the other hand, at high concentrations

of the linear polymer, ν_2 rapidly decreases with increasing ϕ and the linear polymer re-enters the gel phase in this regime. Thus, the gel starts to swell again as the linear polymer concentration increases. Because of the reduction in the number of conformations, linear polymer chains entering the gel phase lose their conformational entropy. Therefore energy gain due to the contact between the linear polymer and PNIPA segments exceeds the loss in the conformational entropy and the chains easily penetrate the PNIPA gel. As shown in Figures 5.2 and 5.3, the gel is swollen state at high concentrations of the linear polymer and the linear polymer concentration in the gel is equal to that in the solution ($\nu_3/\phi = 1$) in polymer melt (ϕ=1). Figure 5.1 and 5.2 also show that both deswelling and reswelling transitions in PNIPA gel take place in a narrow range of linear polymer concentration, inside which the gel is in collapsed state.

Simulated results predict that the behavior of reentrant transition drastically changes depending on a slight change in the χ_{13} values (Figure 5.2); $\chi_{13} \geq 0.063$ gives a smooth reentrant transition, whereas $0.063 > \chi_{13} > 0.03$ predicts first-order collapse and decollapse transitions. For $0.03 > \chi_{13} > -0.11$ one obtains a continuous deswelling of the gel followed by a first-order swelling transition. In the Figure 5.1 and 5.2, the dotted lines illustrate the phase transition regions and the ends of these lines give the composition of the coexisting gel phases. As shown in Figure 5.2, a closed-loop phase boundary can be obtained by combination of the end points of the dotted lines at various χ_{13} values. The PNIPA gel must separate into two phases inside this closed-loop phase boundary which represents a domain of instability. The points A and B shown in Figure 5.2 on the phase boundary correspond to the lower and upper critical points, respectively, i.e., if ϕ<A or ϕ>B only one gel phase exists but for A<ϕ<B, two gel phases may coexist depending on the value of χ_{13}.

It is concluded that the required condition of reentrant phase transition of PNIPA gels at 25 °C is $\chi_{13} \cong 0$, $\chi_{23} = 0$. The reentrant swelling behavior of PNIPA gels in polymer solutions is predicted for small values of χ_{13} because of the competition of two attractive interactions. The competition of two forces attracting the linear polymer component of the system increases the extent of reentrant collapse and decollapse

transitions of PNIPA gels. The segments of linear polymer are attracted both by PNIPA hydrogel (χ_{23}=0) and by water ($\chi_{13} \leq$ 0). The linear polymer-water interactions dominate over the linear polymer-PNIPA interactions at low concentration of the linear polymer. Thus, the polymer mainly remains in the solution phase which is more concentrated than the gel phase. The concentration difference between the inside and outside the gel ($\nu_3 - \phi$) creates an additional osmotic pressure and the gel starts to deswell. On the other hand, at high concentration of linear polymer (ϕ), the linear polymer-PNIPA attraction dominates over the linear polymer-water interactions due to the increasing number of contacts between the segments of linear polymer and PNIPA. As a result, the linear polymer again penetrates the gel and it results in gel swelling.

To confirm the theoretical predictions, the experimental swelling data of PNIPA gels (filled symbols) and PAAm gels (open symbols) in PEG300-water mixture reported in the literature are collected in Figure 5.4 as a function of ϕ [10,46]. As the PEG volume fraction ϕ in the external solution increases from 0 to 0.60, both gels deswell continuously. At ϕ>0.6, PAAm gels continue to deswell while PNIPA gels start to swell again. Since the only difference between the PNIPA and PAAm gels is the existence of isopropyl (IP) groups in PNIPA network, IP groups seem to be responsible for this behavior. PEG is known to be attracted by the PNIPA gel due to the hydrophobic interactions between the IP groups of PNIPA and ethylene groups of PEG. The incorporation of IP groups on the network chains creates attractive interactions between the network and PEG segments. However, PEG is also attracted by water through the hydrogen bonding interactions between water and the ether oxygen of PEG chains. As a result, the competing interactions between PEG-water and PEG-PNIPA result in the reentrant swelling behavior of PNIPA gel. As can be seen from Figure 5.4, the volume of PNIPA gels in PEG melt is larger than that of PAAm gels. This means that the segments of PAAm and PEG repeal each other, so that PAAm gel continuously deswells as the PEG concentration is increased.

Thus, Figure 5.4 shows that the results of the present simulations are in good agreement with the experimental data. Also, the experimental results on the PNIPA

gel in low molecular weight solvent-water mixtures reported by Ishidao et all[11] support our predictions.

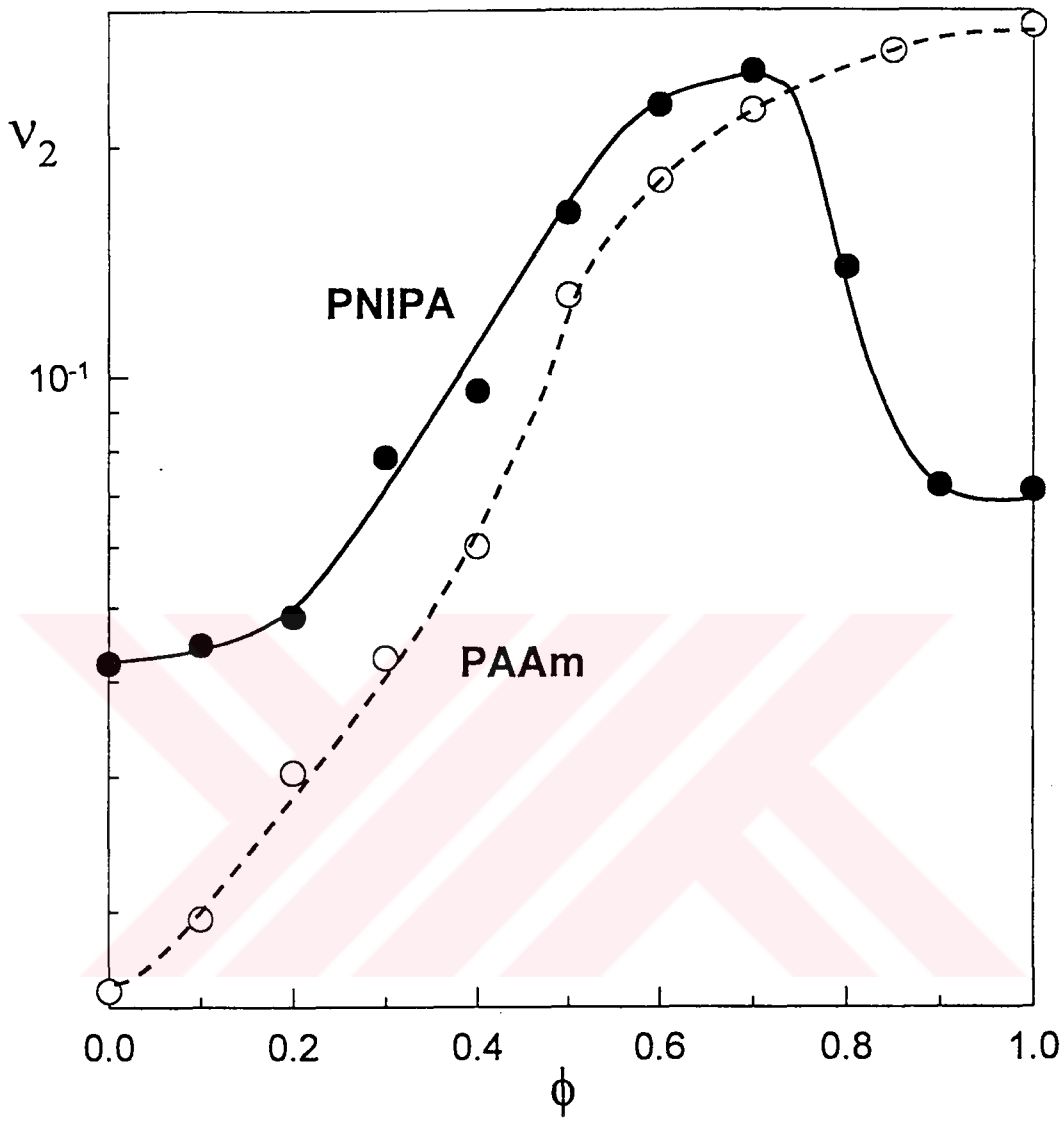

Figure 5.4 The volume fraction of crosslinked polymer in the gel ν_2 shown as a function of PEG-300 concentration ϕ in the external solution. T=298 K

5.2 Effect of Temperature

PNIPA gel exhibits swelling or deswelling transition around its lower critical solution temperature (LCST), which is approximately 34°C in water. Below this temperature the gel is swollen and it shrinks as the temperature is raised. Using Equations (3.36) and (3.37), the equilibrium swelling ratio of non-ionic PNIPA gels (V/V_0) in water was calculated for various temperatures. Calculations were for $\chi_{13} = \chi_{23} = 0$ and χ_{12} parameter was calculated using Equation (4.1). The calculation results are collected in Figure 5.5 as a function of the temperature (T).

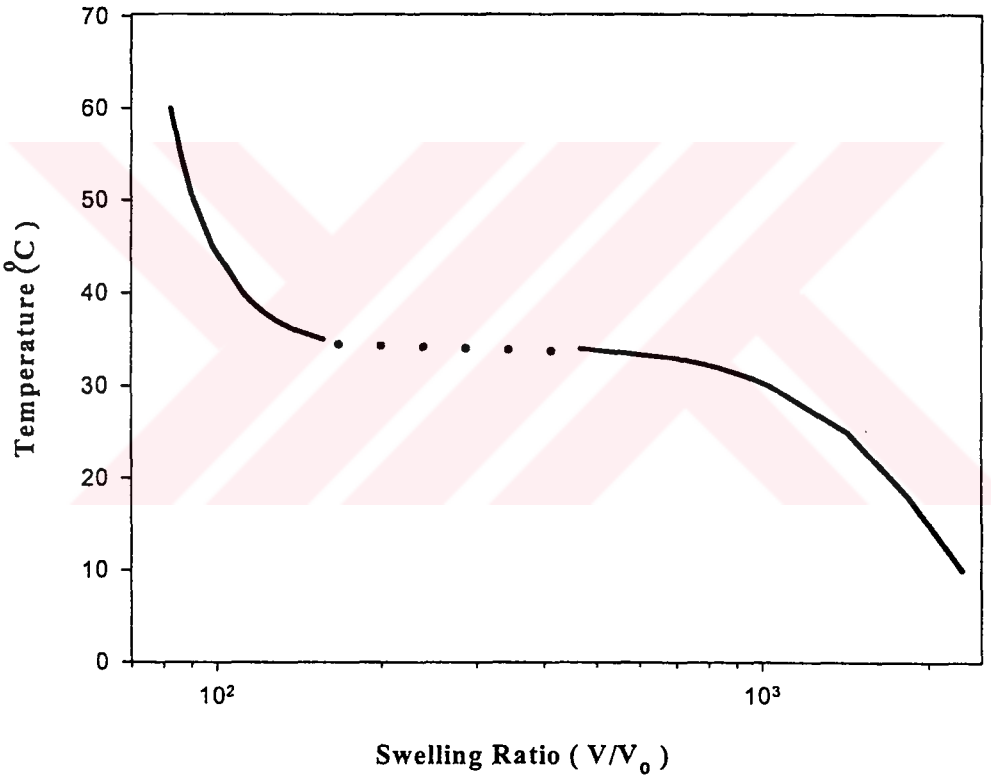

Figure 5.5 Variation of the equilibrium swelling ratio (V/V_0) of PNIPA gels in water with the swelling temperature.

As shown in Figure 5.5, non-ionic PNIPA gels exhibit discrete and reversible volume phase transition in response to an infinitesimal change in temperature. The horizontal dotted line identifies the temperature at which the transition takes place. As expected, the PNIPA gel is in swollen state at low temperatures, while it is in collapsed state at high temperatures. At 34 °C marked with horizontal dotted line, both a swollen and collapsed state can be observed, indicating a first-order volume transition in the gel. The width of the horizontal line at the transition depends on various parameters such as the presence of ionic groups on the network chains, the degree of cross-linking, and the amount of solvent during cross-linking. The results are quite good agreement with the experimental swelling data of PNIPA gels in pure water reported in the literature [17]. Also, similar results to those of Figure 5.5 have been reported by Hirokawa and Tanaka for PNIPA gels[43].

Although PNIPA gel is one of the most studied temperature sensitive gel, the effect of the temperature on the swelling behavior of PNIPA gel in polymer solutions has not been studied before. For the determination of effect of temperature in swelling behavior of non-ionic PNIPA gels in polymer solution, the hydrogel composition as well as the linear polymer partition parameter were calculated for different values of the temperature. For calculations, χ_{23} parameter was set to zero and χ_{12} parameter was calculated using the Equation (4.1) for various temperatures. The ternary plot in Figure 5.6 shows how the PNIPA gel composition varies with temperatures. In the Figures 5.7 and 5.8, the variation of the linear polmer partition parameter and the equilibrium volume fraction of crosslinked polymer in the gel with different values of the temperature are plotted as a function of ϕ. Calculations were for $\chi_{13} = 0$ in Figure 5.7 and $\chi_{13} = 0.05$ in Figure 5.8

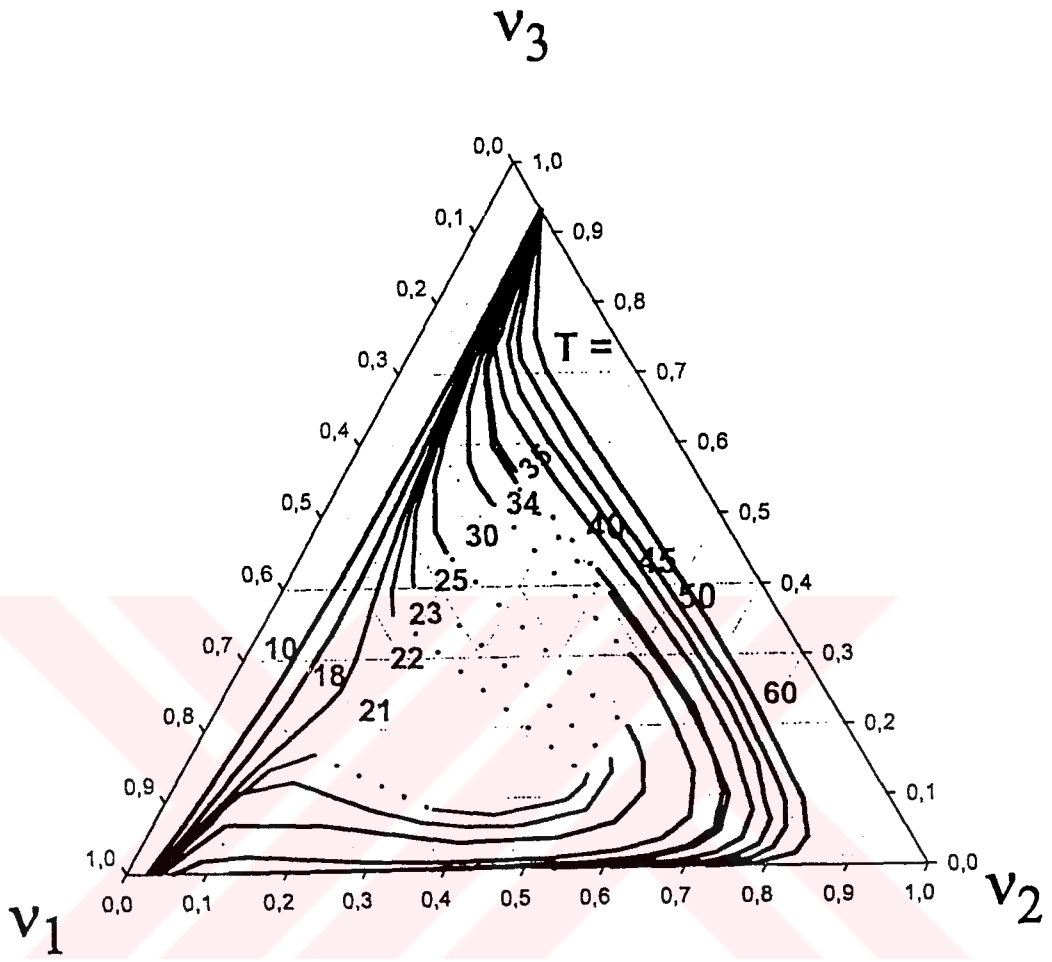

Figure 5.6 Phase diagram for the ternary system PNIPA network – linear polymer – water at various temperatures. $\chi_{13} = \chi_{23} = 0$. Temperatures in ^{0}C are indicated in the Figure.

The simulation results were evaluated in three parts;

1) As shown in Figures 5.7 and 5.8, the gel is in swollen state over the entire range of the linear polymer concentration (ϕ) at temperatures much lower than the LCST of PNIPA (The curves for T=10-21°C in the figures), so that the linear polymer molecules can easily penetrate into the PNIPA gel and the partition parameter is close to unity over the entire range of ϕ.

2) The curves for T= 40-60°C in the figures (5.6)-(5.8) show that PNIPA gel is in collapsed state up to a critical linear polymer concentration (ϕ) at temperatures above its LCST. This is due to the fact that the conformational entropy of the linear polymer in the solution is much higher than that in the collapsed state, so that the linear polymer cannot enter into the collapsed gel. At temperatures above the LCST of PNIPA, the dissociation of ordered water molecules surrounding hydrophobic isopropyl groups of the PNIPA chains prevents the penetration of polymer molecules into the gel at low polymer concentration. As a result, the gel collapses in water. Thus, the linear polymer partition parameter (ν_3/ϕ) is close to zero for the collapsed PNIPA as shown in Figures 5.7 and 5.8. Also, below the critical polmer concentration, the partition parameter is decreasing function of ϕ while ν_3 rapidly increases and approaches to the value of ϕ(The curves for T=22-34°C) and above the critical linear polymer concentration, the collapsed PNIPA gel undergoes a swelling transition which takes place in a narrow range of ϕ due to the favorable linear polymer-PNIPA interactions, required $\chi_{23} = 0$.

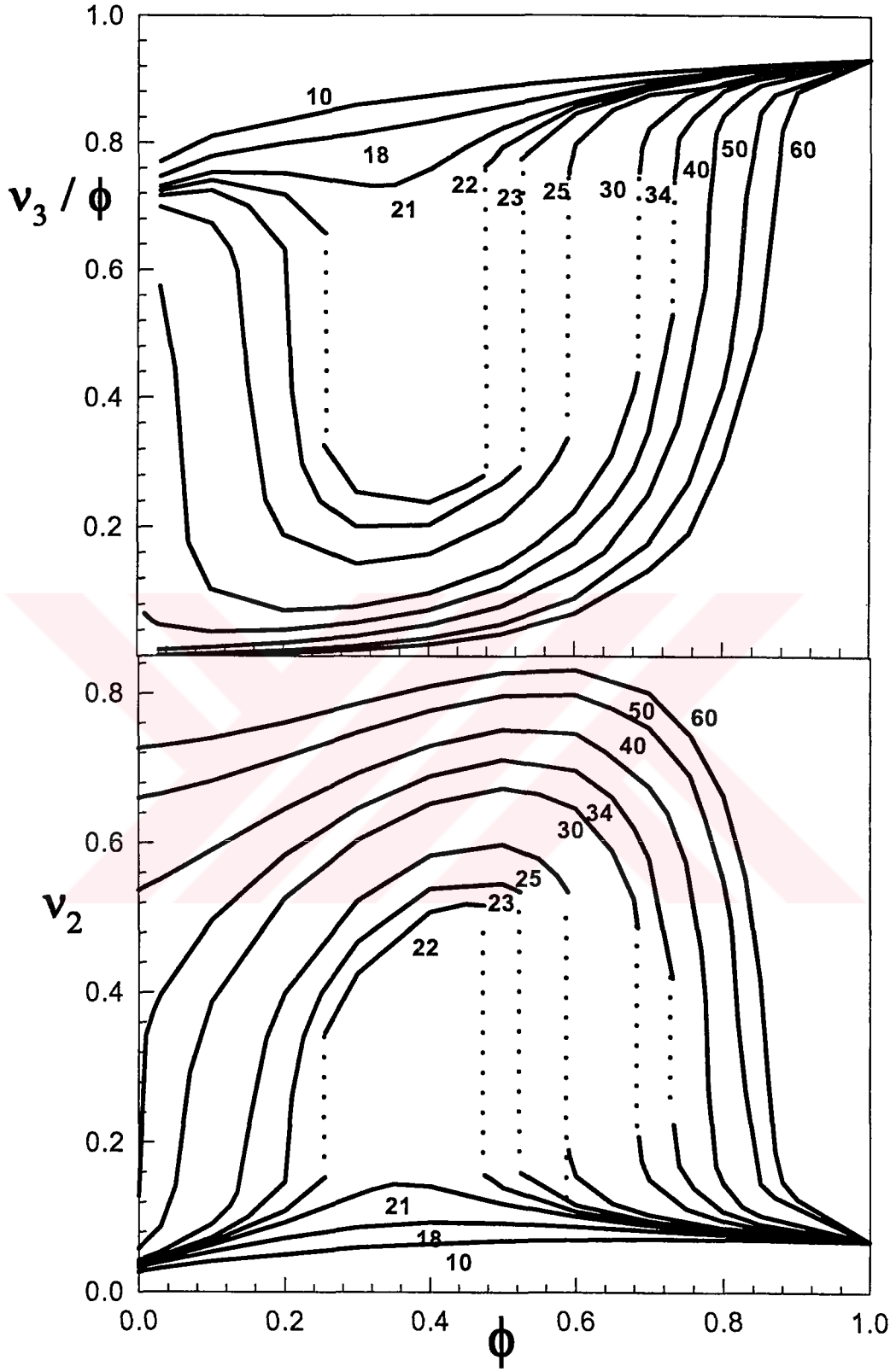

Figure 5.7 Variations of the polymer partition parameter ν_3/ϕ and the volume fraction of crosslinked polymer in the gel ν_2 with the polymer concentration ϕ in the external solution. $\chi_{13} = \chi_{23} = 0$. Temperatures in ^{0}C are indicated in the Figure.

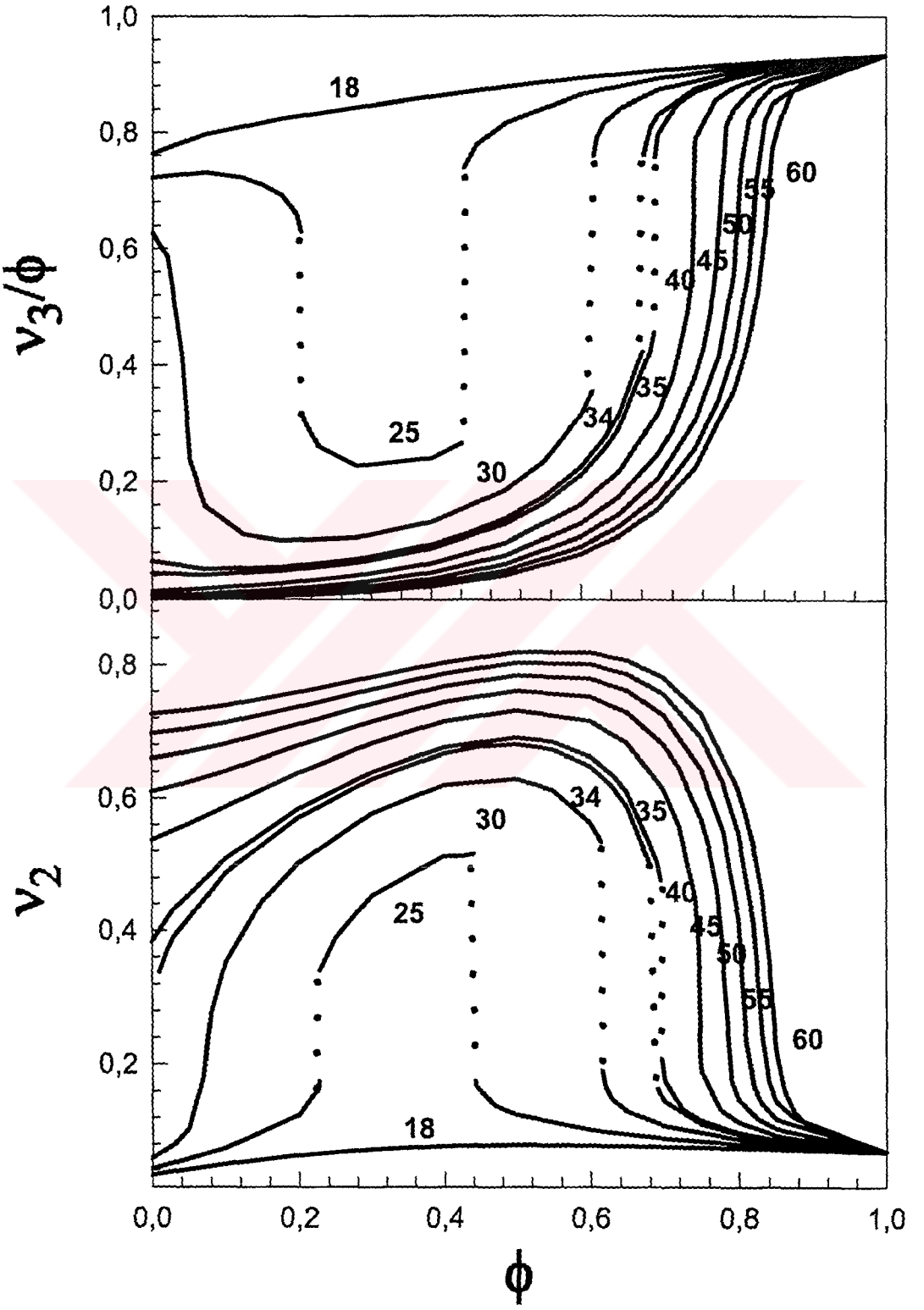

Figure 5.8 Variations of the polymer partition parameter ν_3/ϕ and the volume fraction of crosslinked polymer in the gel ν_2 with the polymer concentration ϕ in the external solution. $\chi_{13} = 0.05, \chi_{23} = 0$. Temperatures in ^{0}C are indicated in the Figure.

Figure 5.9 shows the swelling curves of PNIPA gels for various temperatures calculated for $\chi_{13} = 0.1$ and $\chi_{13} = 0.15$, respectively. It appears from Figures (5.7)-(5.9) that the swelling and deswelling transitions start to appear jumpwise first-order at temperatures very close to the LCST of PNIPA.

3) At temperatures slightly below the LCST of PNIPA, the gel exhibits reentrant phase transition in which the gel collapses once and then reswells as the linear polmer concentration in the external solution is varied monotonically. In Figure 5.10, for various temperatures, the crosslinked polymer volume fraction in the gel v_2 and the linear polymer partition parameter (v_3/ϕ) are plotted as functions of ϕ. Calculations were for $\chi_{13} = 0.2$ and 0.25, respectively. Comparision of Figures (5.7)-(5.10) show that the reentrant behavior starts to appear at 25, 28, and 33°C for $\chi_{13} = 0$, 0.1 and 0.2, respectively. Thus, first-order swelling transitions of the gel occur at higher temperatures as χ_{13} parameter increases while the critical linear polymer concentration required for the swelling transition shifts to smaller values. An island of instability in which the gel separates into two phases is already seen in the figures. Another feature shown in figures is that as the χ_{13} parameter increases, the closed domain of instability shifts to higher temperatures. As shown in Figure 5.10A, at T=55°C, the PNIPA gels exhibit continuous swelling transition which is jumwise first-order in Figure 5.10B

According to Equation (4.1), increasing the temperature of the system also increases the χ_{12} parameter, so that the interaction between the solvent and PNIPA becomes worse. Thus, as the temperature increases, the χ_{13} parameter required for the reentrant behavior of PNIPA gel also increases.

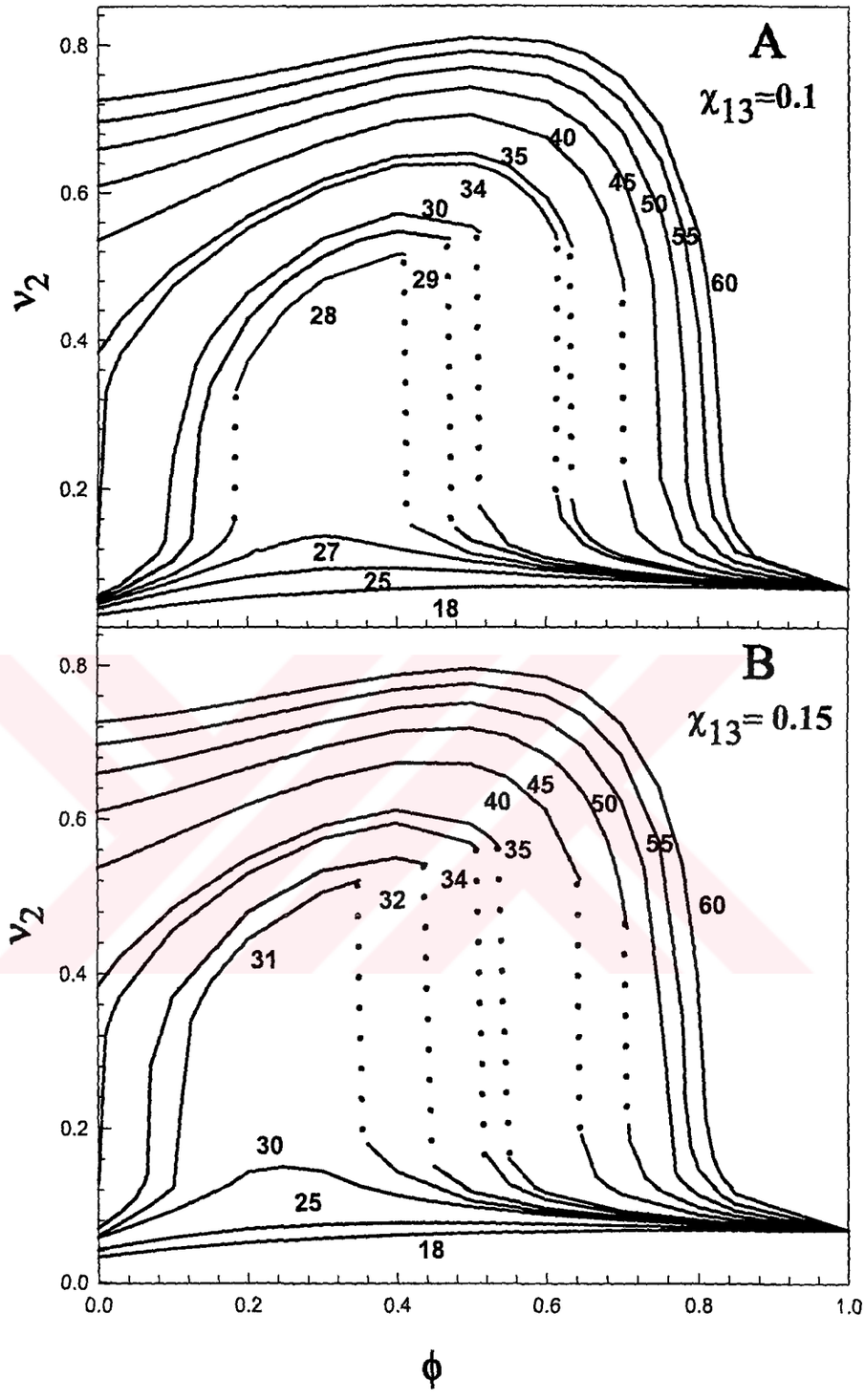

Figure 5.9 Variations of the polymer partition parameter ν_3/ϕ and the volume fraction of crosslinked polymer in the gel ν_2 with the polymer concentration ϕ in the external solution. $\chi_{23}=0$, $\chi_{13}=0.1$ (A) and 0.15 (B). Temperatures in ^{0}C are indicated in the Figure.

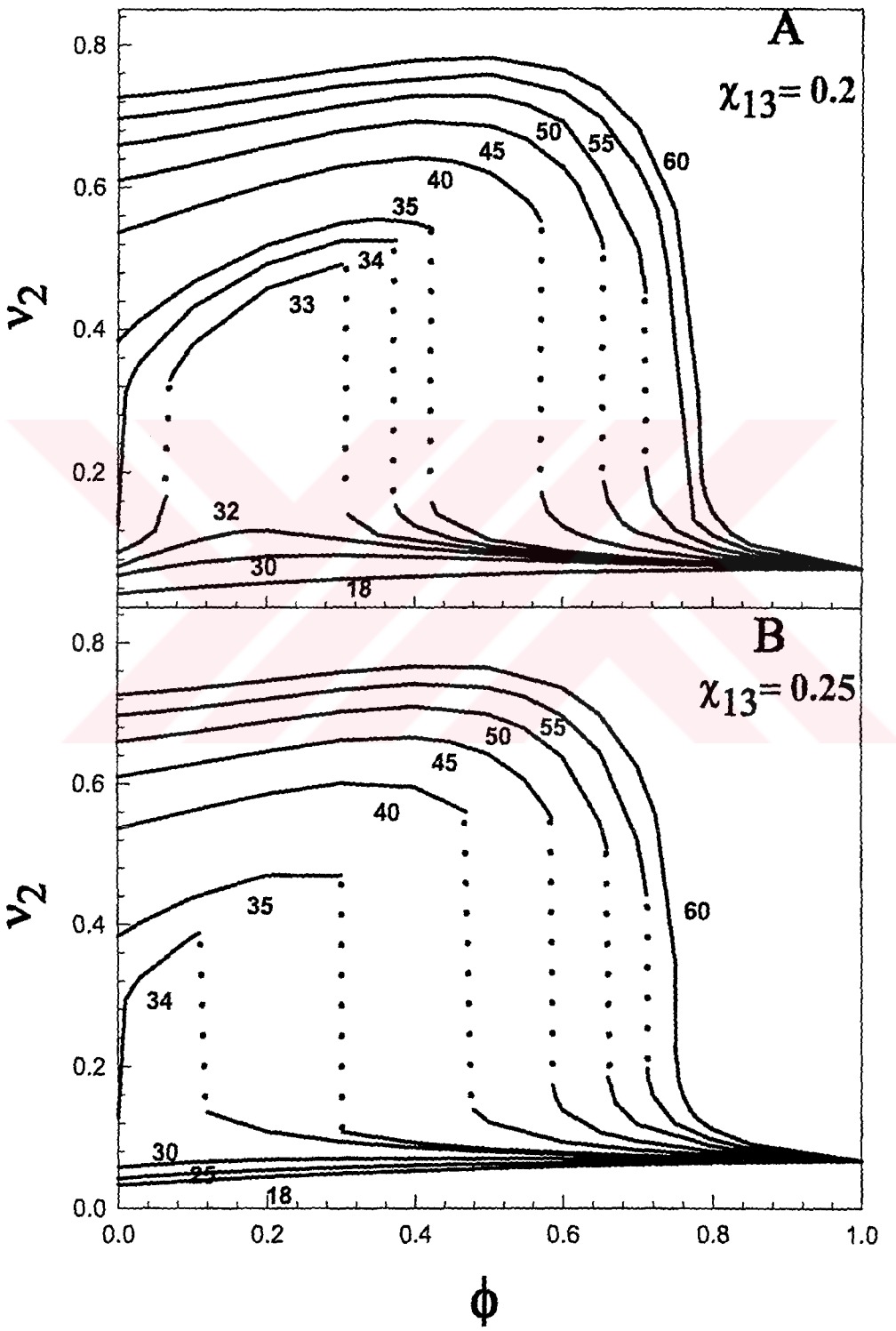

Figure 5.10 Variations of the volume fraction of crosslinked polymer in the gel ν_2 with the polymer concentration ϕ in the external solution. $\chi_{23} = 0$, $\chi_{13} = 0.2$ (A) and 0.25 (B). Temperatures in ^{0}C are indicated in the Figure.

5.3 Effect of The Linear Polymer-PNIPA Interactions

The variation of the volume fraction of crosslinked polymer in the gel (ν_2) and the partition parameter (ν_3/ϕ) with the volume fraction of the linear polymer in the external solution ϕ for various values of linear polymer-PNIPA interaction parameter (χ_{23}) is shown in Figures 5.11 and 5.12. Calculations were for T=25°C and for χ_{13} = 0 and 0.05, respectively. The curves in the figures show that the extent of interaction between the linear polymer and PNIPA is rather sensitive to the value of χ_{13} parameter. Also, the transitions from the swollen to collapsed states and then again to the swollen state occur smoothly or jumpwise first-order depending on the value of χ_{13} parameter.

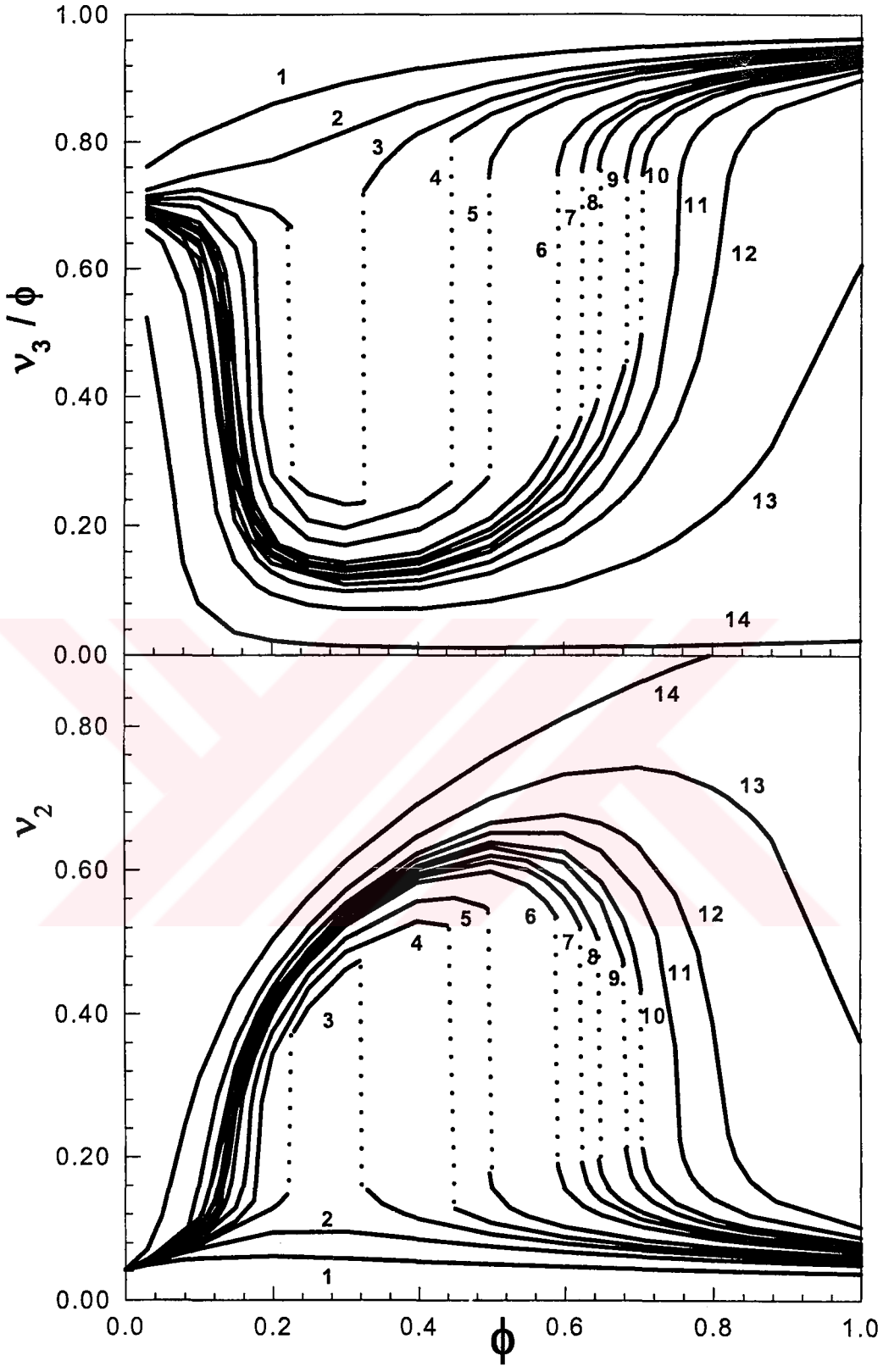

Figure 5.11 The polymer partition parameter ν_3/ϕ and the volume fraction of crosslinked polymer in the gel ν_2 shown as a function of the polymer concentration ϕ in the external solution. χ_{13} = 0, T = 298 K and χ_{23} = - 0.10 (1); -0.04 (2); -0.025 (3); - 0.0175 (4); - 0.01 (5); 0 (6); 0.0035 (7); 0.006 (8); 0.01 (9); 0.0125 (10); 0.018 (11); 0.025 (12); 0.05 (13); 0.20 (14)

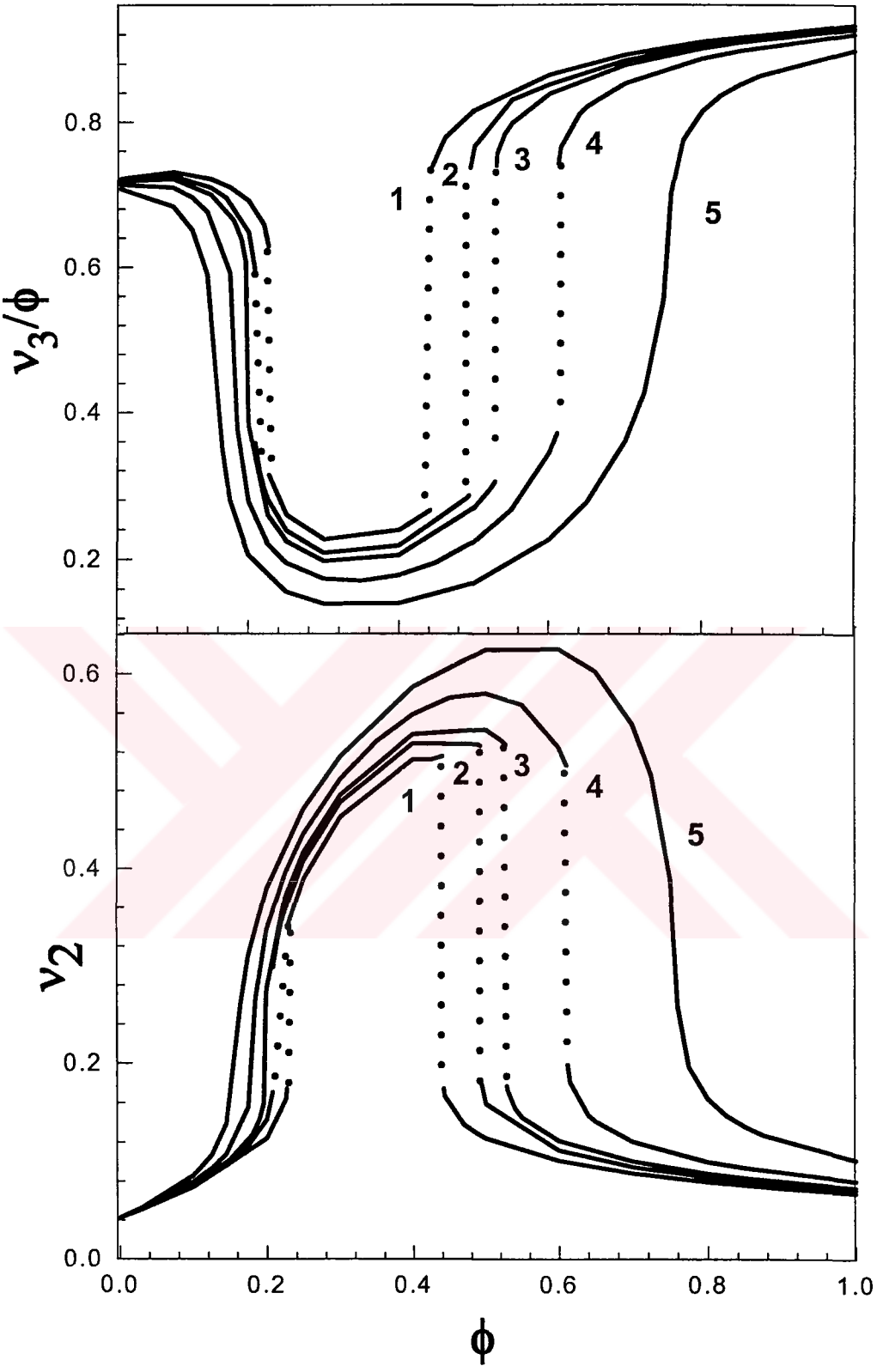

Figure 5.12 The polymer partition parameter ν_3/ϕ and the volume fraction of crosslinked polymer in the gel ν_2 shown as a function of the polymer concentration ϕ in the external solution. χ_{13} = 0.05, T = 298 K and χ_{23} = 0.00 (1); 0.0035 (2); 0.006 (3); 0.0125 (4); 0.025 (5)

Simulated results in the figures are discussed in three parts to determine the effects of the transition behavior of PNIPA gels in polymer solutions;

1) If the value of χ_{23} parameter is much lower than χ_{13} parameter ($\chi_{23} << \chi_{13}$), the attractive interactions between water and the linear polymer becomes worse and the linear polymer-PNIPA attraction dominates over the linear polymer-water interactions. Thus, the linear polymer can easily penetrate into the hdyrogel network and the gel swells as the linear polymer concentration in the solution increases.

2) If the value of χ_{23} parameter is very close to the value of χ_{13} parameter, the linear polymer is attracted both by water and by PNIPA network. The competing interactions between the linear polymer-water and the linear polymer-PNIPA result in the reentrant swelling behavior of the gel. Thus, the required condition of reentrant phase transition in PNIPA gel is $\chi_{13} \cong \chi_{23} \cong 0$ and the higher the χ_{13} parameter the higher the χ_{23} parameter required for the reentrant behavior.

3) If the value of χ_{23} parameter is much higher than the value of χ_{13} parameter ($\chi_{23} >> \chi_{13}$), the attractive interactions between the linear polymer and PNIPA network becomes worse and water attracts the linear polymer stronger than the PNIPA network, so that the linear polymer mainly remains in the solution phase which is more concentrated than the gel phase. As pointed out before, due to the concentration difference between the inside and outside the gel, it starts to deswell monotonically as the external linear polymer concentration increases.

Figure 5.13 shows the variations of the linear polymer partition parameter (ν_3/ϕ) and the volume fraction of crosslinked polymer in the gel (ν_2) with the concentration of the linear polymer in the external solution ϕ for various values of the linear polymer-PNIPA interaction parameter χ_{23}. Calculations were for T=25°C and for χ_{13}= 0.1. It is seen that the volume fraction of crosslinked polymer in the gel increases monotonically (the gel volume ($1/\nu_2$) decreases) while the linear polymer partition parameter is a decreasing function of ϕ as the external polymer concentration increases.

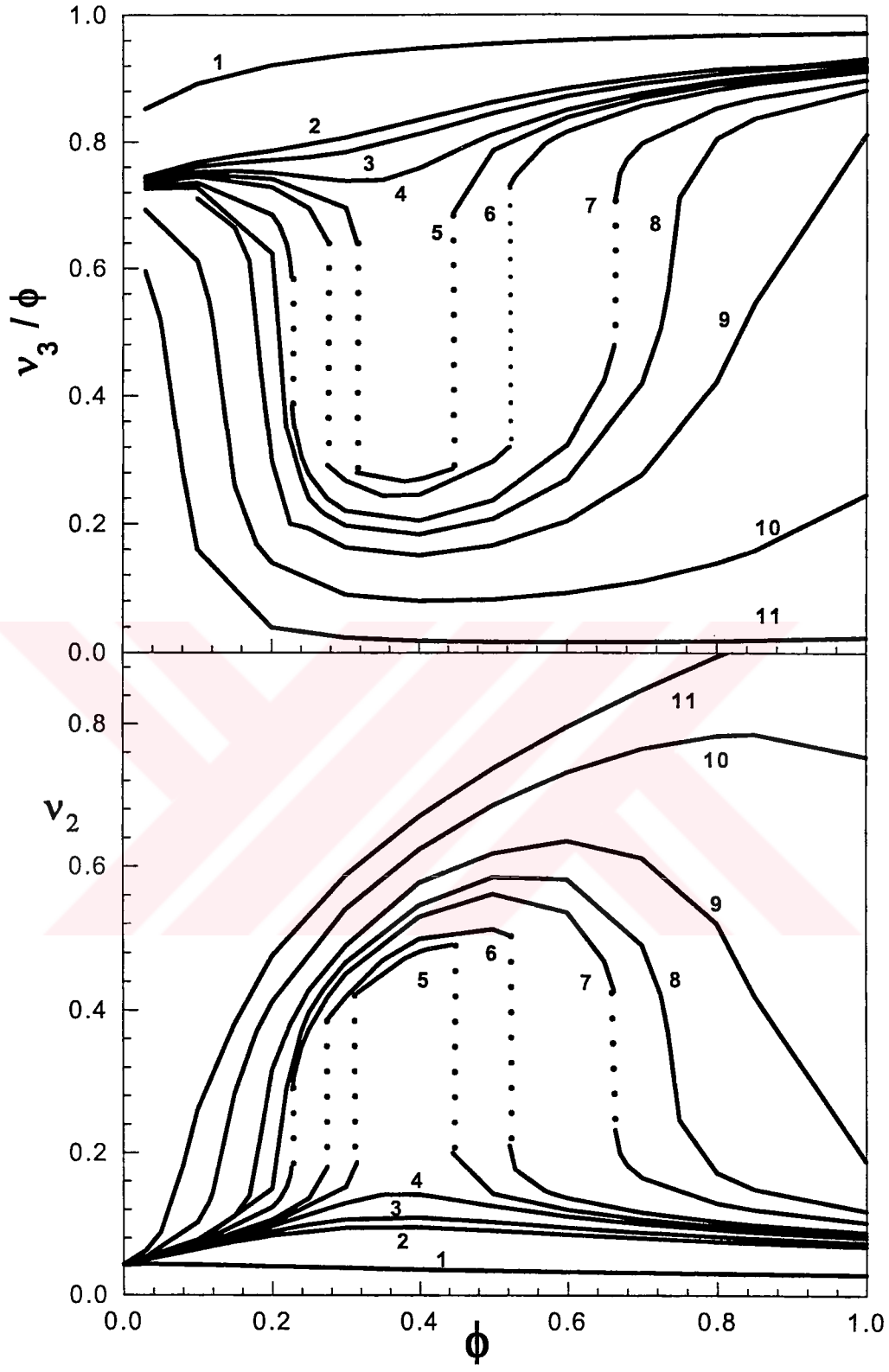

Figure 5.13 The polymer partition parameter ν_3/ϕ and the volume fraction of crosslinked polymer in the gel ν_2 shown as a function of the polymer concentration ϕ in the external solution. χ_{13} = 0.1, T = 298 K and χ_{23} = - 0.20 (1); 0 (2); 0.006 (3); 0.0125 (4); 0.015 (5); 0.018 (6); 0.025 (7); 0.03 (8); 0.04 (9); 0.08 (10); 0.20 (11)

5.4 Effect of The Molecular Weight of Linear Polymer

Figure 5.14 shows the variation of v_2 of non-ionic PNIPA gels with the linear polymer concentration (ϕ) in the external solution for different values of y. Calculations were for T=298 K, $\chi_{13} = 0.05$ and χ_{23}=0. The curves in the Figure indicate that at low values of y (the curve for y=7.35), the gel volume ($1/v_2$) decreases slightly as the external linear polymer concentration increases, so that the linear polymer molecules can easily penetrate the PNIPA gel. At large values of y (the curve for y=100), the linear polymer mainly remains in the solution phase, so that the gel is in collapsed state. However, at intermediate values of y, the PNIPA gel exhibits reentrant phase transition.

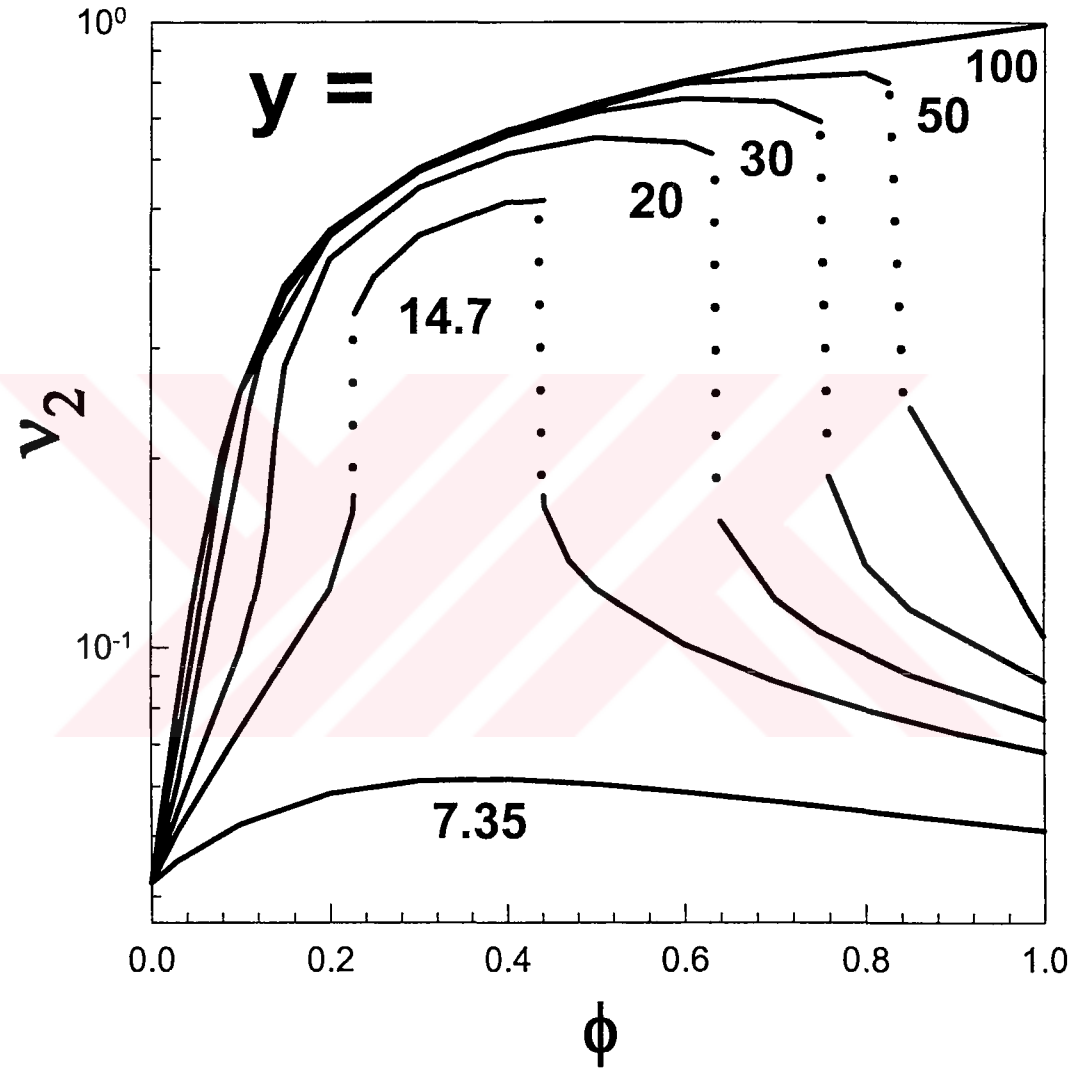

Figure 5.14 The volume fraction of crosslinked polymer in the gel ν_2 shown as a function of the polymer concentration ϕ in the external solution. T = 298 K χ_{13} = 0 and χ_{23} = 0.05. The values of y used in the calculations are indicated in the Figure. The dotted lines represent the phase transition regions.

5.5 Effect of The Charge Density of PNIPA gels

In Figures 5.15 and 5.16, the volume fraction of the crosslinked polymer in the gel (ν_2) and the partition parameter of the linear polymer (ν_3/ϕ) were plotted as a function of the linear polymer concentration (ϕ) in the external solution. The charge densities of the networks are indicated in the Figures. Calculations were for χ_{13}=0 and 0.05, respectively. In these calculations, the free energy term representing the contribution from the translational entropy of counterions (Equation (2.25)) was also taken into account.

As expected[30], ionic gels swell ($\phi = 0$) in water much more than the neutral gel due to the simultaneous increase of the mobile counterion concentration inside the gel because of the condition of electroneutrality. The concentration difference of the mobile ions between the inside and outside the gel creates an additional osmotic pressure that swells the gel. The results of calculations for ionic gels indicate that, if f is higher than a certain value ($10^2 f = 0.1$), the ionic gel remains in the swollen state over the entire range of the external linear polymer concentration. The high swelling behavior of ionic gels is also reflected in the calculated ν_3/ϕ ratios, which are always close to unity. For higher charge densities, the osmotic pressure of counterions inside the gel increases the gel volume, so that the linear polymer chains can easily penetrate into the PNIPA network without an essential loss of their conformational entropy and can interact with water inside the gel phase. As a result, the gel remains in the swollen state over all ϕ values. Figures 5.15 and 5.16 also show that for very small charge densities (the curves for f=0.0005 and 0.001) PNIPA gels exhibit first-order reentrant phase transition and the extent of the transition increases as the network charge density decreases.

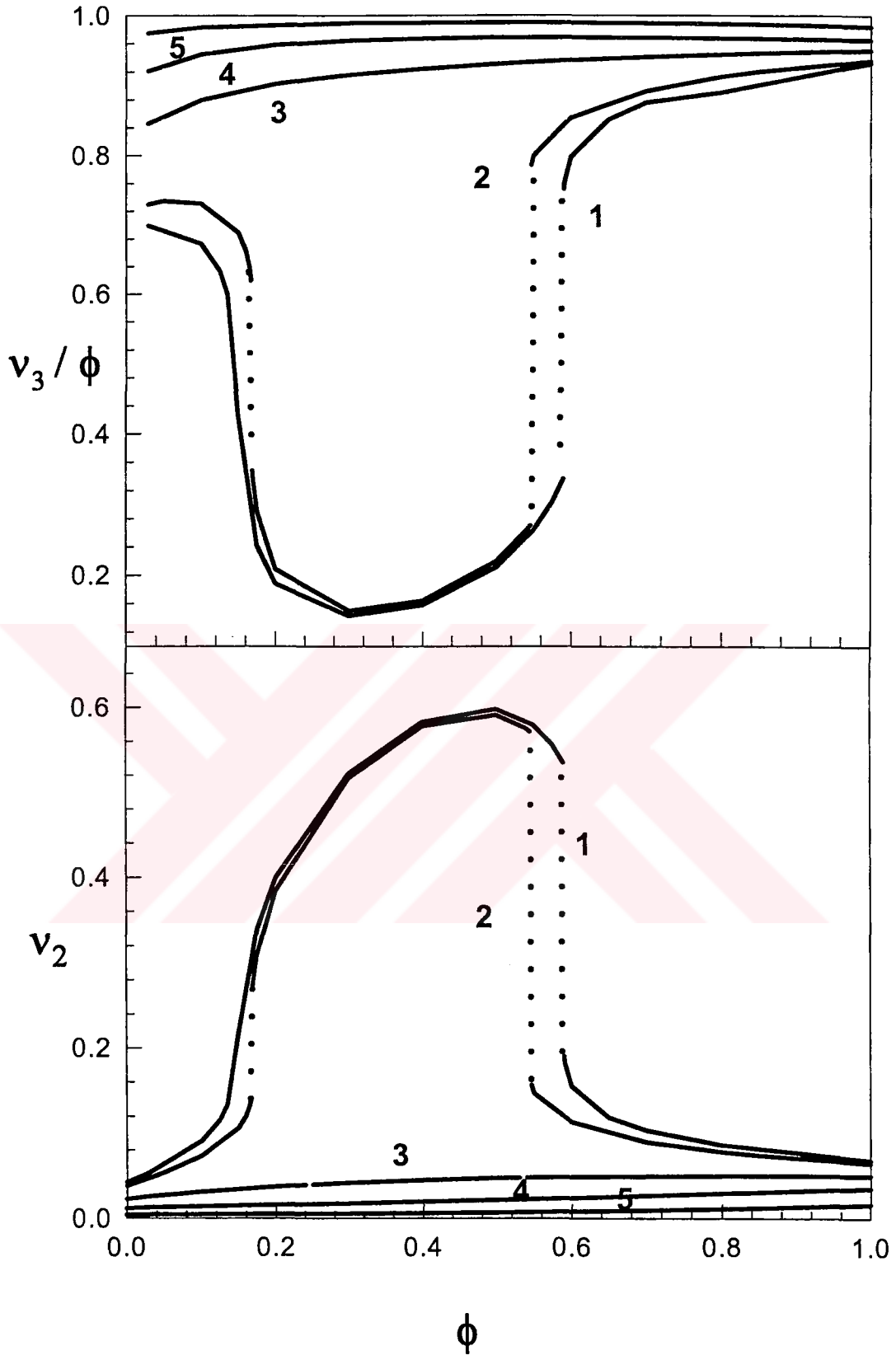

Figure 5.15 The polymer partition parameter ν_3/ϕ and the volume fraction of crosslinked polymer in the gel ν_2 shown as a function of the polymer concentration ϕ in the external solution. $\chi_{13} = \chi_{23} = 0$, T = 298 K and $10^2 f_0 = 0$ (1); 0.1 (2); 0.6 (3); 1.3 (4); 3.3 (5).

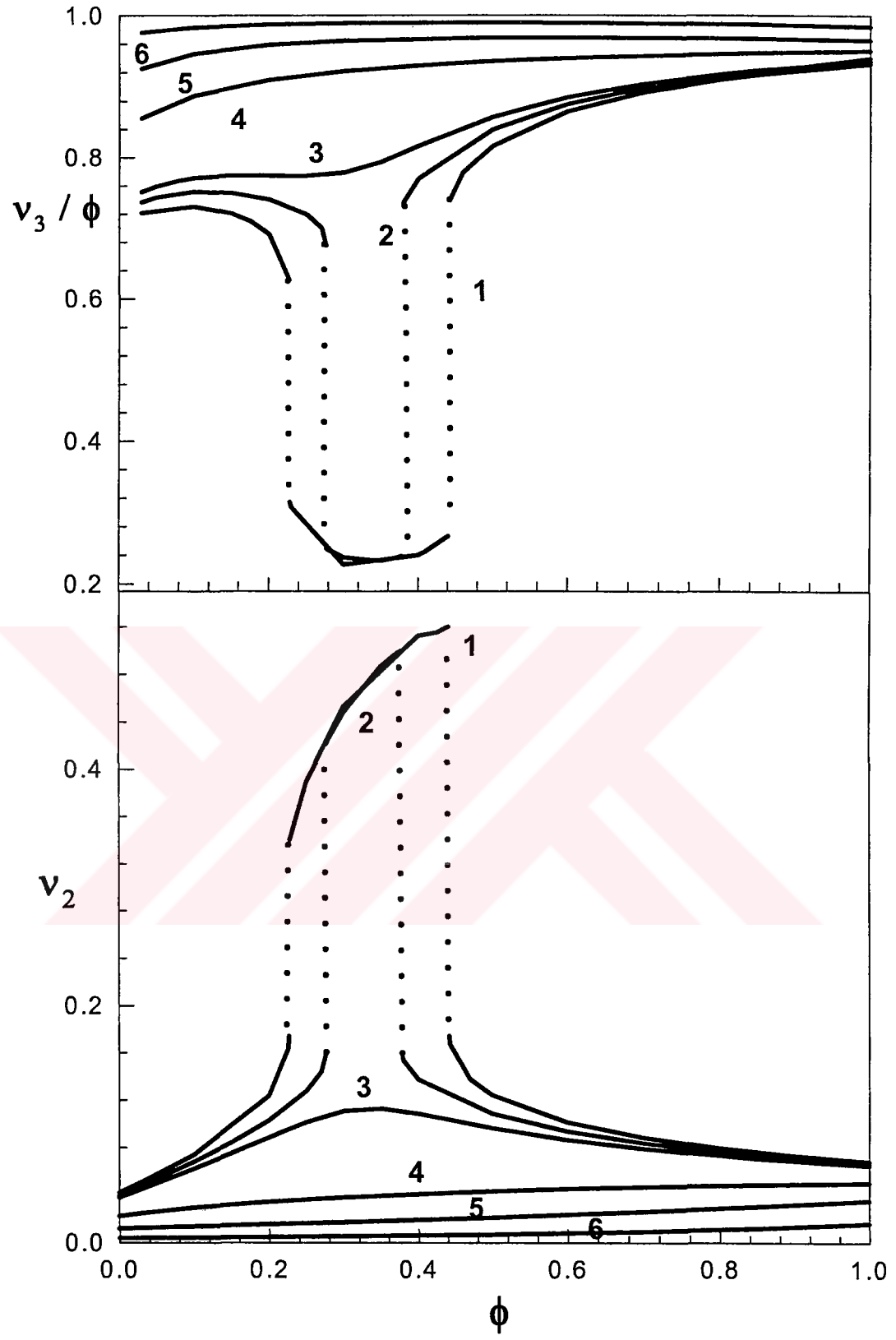

Figure 5.16 The polymer partition parameter ν_3/ϕ and the volume fraction of crosslinked polymer in the gel ν_2 shown as a function of the polymer concentration ϕ in the external solution. $\chi_{13} = 0.05$, $\chi_{23} = 0$, T = 298 K and $10^2 f_0 = 0$ (1); 0.05 (2); 0.1 (3); 0.6 (4); 1.3 (5); 3.3 (6).

To confirm the theoretical predictions, the experimental swelling data of PNIPA gels with different amount of ionizable groups (2-acrylamido-2-methylpropanesulfonic acid sodium salt, AMPS) were collected in Figure 5.17 plotted as a function of the volume fraction of PEG-300 in the external solution[10]. It is seen that the PNIPA gel without any ionizable group exhibits reentrant phase transition. However, the ionic gels with 3 and 10 mol-% AMPS remain in the swollen state over the entire range of PEG. Thus, our simulation results shown in Figures 5.15 and 5.16 are in accord with the experimental results.

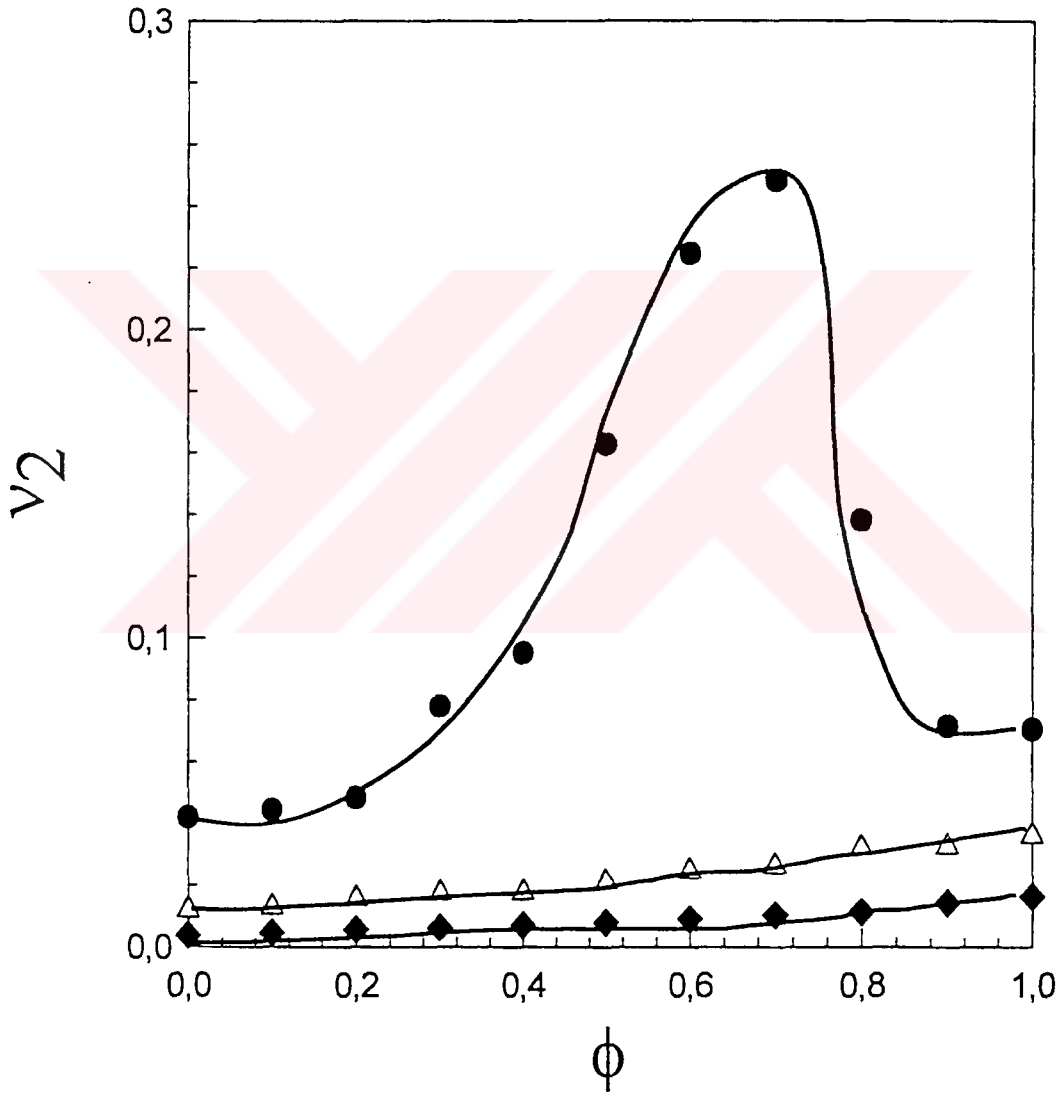

Figure 5.17 The volume fraction of crosslinked polymer in the gel ν_2 shown as a function of the PEG - 300 concentration ϕ in the external solution. T = 298 K. Experimental data were taken from the literature [8]. PNIPA gel with 0 (•), 3 (Δ) and 10 mol % AMPS (♦). The curves only show the trend of data.

6. CONCLUSIONS AND RECOMMENDATIONS

The present work was carried out to predict the swelling behavior of PNIPA gels in aqueous polymer solutions. The conclusions that can be drawn from the simulated results can be summarized as follows;

The non-ionic PNIPA gels show reentrant phase transition in aqueous solutions of low molecular weight linear polymers due to the competition of two forces attracting the linear polymer molecules. For repulsive interactions between the linear polymer and water, the gel remains in the swollen state over the entire range of the linear polymer concentration (ϕ), while for attractive interactions between the linear polymer and water, the gel exhibits reentrant phase transitions. It can be seen from the Figure 5.2 that the transitions from the swollen to collapsed states and then again to the swollen state occur smoothly or jumpwise first-order depending on a slight change in the χ_{13} value.

The effect of the temperature on the swelling behavior of PNIPA gels in the polymer solutions was theoretically evaluated. The simulated results indicate that at temperatures slightly below the LCST of PNIPA, the gel exhibits reentrant phase transition. Moreover, at temperatures above the LCST of PNIPA, the gel is in collapsed state up to a critical polymer concentration and it shows a continuous or discontinuous swelling transition above the critical linear polymer concentration. Decreasing the temperature of the system shifts the critical polymer concentration required for the swelling transition to smaller values.

The swelling behavior of PNIPA gels immersed in aqueous solutions of the linear polymer with different molecular weights was also investigated and it was found that the equilibrium volume fraction of crosslinked polymer in the gel (ν_2) increases as the number of segments in the linear polymer (y) increases and the gel collapses at

sufficienly large values of y. If the linear polymer chains are short enough (y=7.35), a large amount of PEG can penetrate into the gel.

The simulation results for ionic PNIPA gels immersed in aqueous polymer solutions indicate that if the charge density f is sufficiently high, the gel remains in the swollen state over the entire range of the linear polymer concentration. A first-order reentrant phase transition is observed only if f exceeds a critical value.

For future studies, theoretical calculations may be performed to present a method of computation for phase equilibrium in multicomponent polymer solutions based on the F-H theory and to show how interaction parameters and molecular weights affect the polymer compatibility.

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APPENDIX A

Computer Program for Theoretical Calculation of Equilibrium Volume Fraction of Crosslinked Polymer in Gel (ν_2) and Linear Polymer Partition Parameter (ν_3/ϕ)

Calculation of the equilibrium volume fraction of crosslinked polymer in the gel and the linear polymer partition parameter:

```
   DIM SS(15000), NN(15000), E9(15000)
   CLS
   GOSUB BASLIK:
   Y# = 14.7:      '****************** DEGREE OF POLYMERIZATION OF
   LINEAR CHAINS
   V20# = .06: '
   V2W# = .042
   FF# = 0: ' MOLE FRACTION OF IONIC UNITS IN THE NETWORK
   NNN# = 172: '     = (RO/Mc)V1   DEGREE OF POLYM. OF NETWORK
   CHAINS
   T = 304
   '
   KAI13 = .15                '          INTERACTION PARAMETERS
   ' 1= S  2= PN  3 = LP
   KAI23 = 0
   '
   PSI# = .11: '  VOLUME FRACTION OF LINEAR POLYMERS IN THE
   SOLUTION
   V3# = .0475
20  V3# = V3# + .000001
   DEF FNF1# (X#) = (1 / NNN#) * (V20# ^ (2 / 3) * X# ^ (1 / 3) - X# / 2) +
   LOG((1 - X# - V3#) / (1 - PSI#)) + X# + V3# - PSI# - (V3# - PSI#) / Y# + (3.415
   - 902.2 / T + .518 * X#) * X# ^ 2 + KAI13 * (V3# ^ 2 - PSI# ^ 2) + ((3.415 -
   902.2 / T + .518 * X#) + KAI13 - KAI23) * X# * V3# - X# * FF#

   DEF FNF2# (X#) = -LOG((1 - X# - V3#) / (1 - PSI#)) + (1 / Y#) * LOG(V3# /
   PSI#) + 2 * KAI13 * (PSI# - V3#) + (KAI23 - KAI13 - (3.415 - 902.2 / T + .518 *
   X#)) * X#
 '
 '
   BAS# = .000001#: BITT# = .000092: HASSAS = .0000001#
50  BASY1# = FNF1#(BAS#): BITTY2# = FNF1#(BITT#)

   IF SGN(BASY1#) = -SGN(BITTY2#) THEN 200
   UZUN# = (BITT# - BAS#) / 10
   FOR BASAMAK = 1 TO 9: BASY9# = FNF1#(BAS# + BASAMAK * UZUN#)


   IF SGN(BASY9#) = SGN(BASY1#) THEN 100
   BITT# = BAS# + BASAMAK * UZUN#: GOTO 200
100  NEXT BASAMAK
   BITT# = BITT# + .1: GOTO 50
200  BASY1# = FNF1#(BAS#)
   BITTY2# = FNF1#(BITT#)

   IF ABS(BITT# - BAS#) < ABS(HASSAS) THEN v21# = .5 * (BAS# + BITT#):
   GOTO 300
```

```
   ORTA# = .5 * (BAS# + BITT#)
   ORTAY3# = FNF1#(ORTA#)

   IF SGN(ORTAY3#) = SGN(BASY1#) THEN BAS# = ORTA#: GOTO 200
   BITT# = ORTA#: GOTO 200
300
   '
   '
   '
   BAS# = .000001#: BITT# = .002136
350  BASY1# = FNF2#(BAS#): BITTY2# = FNF2#(BITT#)
   IF SGN(BASY1#) = -SGN(BITTY2#) THEN 500
   UZUN# = (BITT# - BAS#) / 2
   FOR BASAMAK = 1 TO 9: BASY9# = FNF2#(BAS# + BASAMAK * UZUN#)

   IF SGN(BASY9#) = SGN(BASY1#) THEN 400
   BITT# = BAS# + BASAMAK * UZUN#: GOTO 500
400  NEXT BASAMAK
   BITT# = BITT# + .1: GOTO 350
500  BASY1# = FNF2#(BAS#)
   BITTY2# = FNF2#(BITT#)
   IF ABS(BITT# - BAS#) < ABS(HASSAS) THEN v22# = .5 * (BAS# + BITT#):
   GOTO 600

   ORTA# = .5 * (BAS# + BITT#)
   ORTAY3# = FNF2#(ORTA#)

   IF SGN(ORTAY3#) = SGN(BASY1#) THEN BAS# = ORTA#: GOTO 500
   BITT# = ORTA#: GOTO 500
600  JJJ = JJJ + 1
   IF JJJ < 30 THEN GOTO 601
   JJJ = 0
   '
       ************************************************************
       *****
   ZZZ = ZZZ + 1
   IF ZZZ > 21 THEN GOSUB BASLIK:
   PRINT USING "##.####^^^^    "; v21#, v22#, ABS(v21# - v22#), V3#, V20# /
       ((v21# + v22#) / 2)
601
   IF ABS(v21# - v22#) > HASSAS THEN GOTO 20
   PRINT : PRINT
   PRINT "   V3 =     V3/PSI=       V2 =              V/VW=       V/Vo =  "
   PRINT USING "##.#####^^^^    "; V3#, V3# / PSI#, (v21# + v22#) / 2, V2W# /
       ((v21# + v22#) / 2), V20# / ((v21# + v22#) / 2)
   REM  3= 1g  4=1s
   DEF FNF3# (X#) = (1 / NNN#) * (V20# ^ (2 / 3) * X# ^ (1 / 3) - X# / 2) +
       LOG(1 - X# - V3#) + X# + V3# - V3# / Y# + ((3.415 - 902.2 / T + .518 *
       X#) * X# + KAI13 * V3#) * (X# + V3#) - KAI23 * X# * V3# - X# * FF#
```

```
DEF FNF4# (X#) = LOG(1 - PSI#) + PSI# - PSI# / Y# + KAI13 * PSI# ^ 2

REM  5=3g  6=3s
DEF FNF5# (X#) = ((1 / NNN#) * (V20# ^ (2 / 3) * X# ^ (1 / 3) - X# / 2) + (1 /
Y#) * LOG(V3#) + (1 - V3#) / Y# - (1 - X# - V3#) + KAI13 * (1 - X# - V3#) * (1
- V3#) - (3.415 - 902.2 / T + .518 * X#) * X# * (1 - X# - V3#) + KAI23 * X# * (1
- V3# )) - X# * FF#

DEF FNF6# (X#) = (1 / Y#) * LOG(PSI#) - (1 - PSI#) + (1 - PSI#) / Y# + KAI13
* (1 - PSI#) ^ 2

REM  ************************************************************
REM            7 = FREE ENERGY PER LATTICE SITE per RT
REM  ************************************************************
DEF FNF7# (X#) = (1 - X# - V3#) * LOG(1 - X# - V3#) + (V3# / Y#) *
LOG(V3#) + (3.415 - 902.2 / T + .518 * X#) * (1 - X# - V3#) * X# + KAI13 * (1
- X# - V3#) * V3# + KAI23 * X# * V3# + (3 / 2) * (1 / NNN#) * X# * ((V20# /
X#) ^ (2 / 3) - 1 - LOG ((V20# / X#) ^ (1 / 3))): ' + X# * FF# * LOG(X# * FF#)

REM ************************************************************
REM            8 = 2g CHEM POT OF NETWORK SEGMENTS
REM
    ************************************************************
DEF FNF8# (X#) = -(1 / NNN#) * (V20# ^ (2 / 3) * X# ^ (1 / 3) - X# / 2) * (1 -
X#) / X# - (1 - X# - V3#) - V3# / Y# + (3.415 - 902.2 / T + .518 * X#) * (1 - X# -
V3#) ^ 2 + KAI23 * V3# ^ 2 + ((3.415 - 902.2 / T + .518 * X#) + KAI23 -
KAI13) * V3# * (1 - X# - V3#): _

' + FF# * (1 - X# + LOG(X# * FF#))

VOR# = .5 * (v21# + v22#)
VVVVV# = (FNF7#(VOR#) - FNF3#(VOR#) * (1 - V3# - VOR#) -
FNF5#(VOR#) * V3#) / VOR#

PRINT
PRINT " Chem. pot. of network segments = "; : PRINT USING "##.####^^^^  ";
    FNF8#(VOR#), VVVVV#
PRINT
PRINT " Gibbs free enrgy per site       = "; : PRINT USING "##.####^^^^  ";
FNF7#(VOR#)
END

BASLIK: CLS : ZZZ = 0
 PRINT " V2 (1.eq)    V2 (2.eq)     DELTA(V2)      V3        V3/PSI
  V/Vo  "
 RETURN
```

BIOGRAPHY

Nermin GÜNDOĞAN was born in Balıkesir in 1975. She graduated from Istanbul Technical University, Department of Chemistry in 1999 and Mathematics Engineering in 1998.

She was registered as a M.Sc. student to the Institute of Science and Technology of Istanbul Technical University in 1999.

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