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Quantifying the influence of cross-linking percentage on polymer-solvent interactions using the Flory-Huggins model in PVA pervaporation membranes

Mandavalli D. S. V. J. P. Koteswari [1,2,*] and Suggala V. Satyanarayana [3]

[1] *Department of Chemical Engineering, Faculty of Engineering, University of Rajiv Gandhi University of Knowledge Technologies, Rajiv Knowledge Valley, Idupulapaya, 516330, Andhra Pradesh, India*
[2] *Department of Chemical Engineering, Research Scholar, University of Jawaharlal Nehru Technological University Anantapur, Anantapuram 515002, Andhra Pradesh, India*
[3] *Department of Chemical Engineering, Faculty of Engineering, University of Jawaharlal Nehru Technological University Anantapur, Anantapuram 515002, Andhra Pradesh, India*

* *Corresponding author at: Department of Chemical Engineering, Faculty of Engineering, University of Rajiv Gandhi University of Knowledge Technologies, Rajiv Knowledge Valley, Idupulapaya, 516330, Andhra Pradesh, India.*
e-mail: koteswarimandavalli7@gmail.com (M.D.S.V.J.P. Koteswari).

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ABSTRACT

Poly(vinyl alcohol) (PVA) membranes are popular in pervaporation, where interaction between polymers and solvents and the level of cross-linking have a significant effect on swelling, sorption, and transport behavior. The swelling behavior of chemically cross-linked polyvinyl alcohol membranes in various solvents in the presence of two cross-linking agents, including glutaraldehyde and maleic acid, was methodically studied. The equilibrium swelling was used to estimate the Flory-Huggins interaction parameter (χ), which is a measure of the thermodynamic affinity between the polymer network and the penetrant molecules. This parameter is particularly important in pervaporation simulations, where the parameter χ is an expression of the thermodynamic affinity of the solvent and polymer in the membrane phase, which is directly related to the behavior of solvent sorption and can be applied to explain permeation fluxes in solution diffusion-like transport models. The degree of equilibrium swelling was clearly correlated with the percent and the type of cross-linking agent, which allowed correlating χ with the degree of cross-linking density. The results indicate that the swelling ratio and the corresponding values of χ are affected by the type of crosslinker, the degree of cross-linking, and the character of the solvent-polymer system, so different behaviors are found in the acidic and alcoholic solvents. The correlations developed in this work provide reliable information on Flory-Huggin's interaction parameter for use in pervaporation sorption and contribute to the rational design and optimization of cross-linked PVA membranes for separation applications.

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1. Introduction

Hydrophilic membrane has frequently been employed in various alternative membrane-based separation technologies in recent years because of the high energy requirement in the traditional separation technologies. An example is its application in pervaporation to dehydrate organic solvents and in a variety of vapor permeation technologies to remove water vapor from other gases [1]. Furthermore, the polymer side chain has numerous OH groups that make PVA highly water-soluble. The polymer side chain has numerous OH groups that make PVA highly water soluble. PVA membranes always deteriorate in terms of mechanical strength due to swelling in aqueous solutions despite a long-term operation [2-4]. The presence of a crosslinker in the polymeric PVA matrix is established to enhance the mechanical strength [5]. In addition to that, PVA crosslinking enables enhanced thermal stability and material isolation ability [6,7]. Various cross-linking techniques with cross-linking agents such as glutaraldehyde [8,9], maleic acid [10,11], succinic acid [12,13], formaldehyde [14], citric acid [15], sulfosuccinic acid [16], maleic anhydride [17], and boric acid [18] have been explored to be used as a pervaporation membrane, nanofiltration, and other treatments [4,19]. Cross-linking causes chains to be permanently linked in a covalent bond, which reduces solvent uptake and stabilizes the size of the membrane. However, uncross-linked polyvinylidene swells by more than 300-500 percent, but cross-linked membranes usually swell by 15-50 percent. Mechanical and thermal stability is also improved by cross-linking, but too much cross-linking has the advantage of lowering the permeation flux, so the density of cross-linking is delicate to optimize [2,7].

The choice of the polymers to be used in the separation is largely determined by three key factors; the polymer must be highly chemically resistant (compatibility), the sorption capacity, and the excellent mechanical strength in the solution. The polymer must be able to interact well, more preferably with one of the constituents of the mixture, in order to be separated effectively. The Flory-Huggins theory offers a basic explanation of the interactions between the polymer and the solvent in

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terms of the interaction parameter (χ) which can be used to measure the compatibility of the components with the polymer. In polymer systems, the mixing entropy is relatively small; therefore, the enthalpic interaction term represented by χ plays a significant role in determining the Gibbs free energy of mixing. Consequently, the value of χ reflects polymer–solvent compatibility and correlates with the observed swelling behavior and phase stability [20-22].

In hydrophilic polymer membranes such as cross-linked poly(vinyl alcohol) (PVA), χ is very sensitive to penetrant polarity, hydrogen bonding strength, temperature, and is cross-link density and therefore is an important influential factor in swelling thermodynamics and sorption equilibria [22-24]. Reduced values of χ give positive polymer penetrant interactions and better sorption and swelling, while increased χ values denote low affinity and minimal penetrant uptake, which are very important to membrane transport, selectivity and mechanical stability. In addition to being a conceptual parameter to explain polymer-penetrant thermodynamics, χ is also a useful design parameter to predict and optimize the performance of sorption, diffusion, and separation in pervaporation membranes. It is particularly important in sorption and pervaporation modeling because it provides a direct correlation between thermodynamic interactions and the performance of mass transfer. χ is usually determined experimentally by measuring swelling using Flory-Rehner theory, or sorption isotherms, inverse gas chromatography, and osmotic pressure [22,23]. χ is commonly assumed constant in a given polymer-solvent system to simplify the mathematical model in numerous experimental and modeling studies [25]. Although this assumption is convenient, it ignores experimentally determined dependencies of χ on solvent uptake, polymer composition, and network structure that result in the inaccuracies in prediction of thermodynamic driving forces. Some studies have proposed composition-dependent expressions in the form of power law [26] or non-linear expressions [27]; but these have rarely been critically compared with simpler linear approximations. In addition, there has been little research on regression-based comparison of linear and nonlinear correlations of crosslinker concentration, swelling ratio, solvent volume fraction, and interaction parameter in the literature.

To fill this gap, the present study integrates equilibrium swelling experiments with Flory–Huggins analysis to establish the dependence of the interaction parameter (χ) on cross-linker concentration and solvent volume fraction in chemically cross-linked PVA membranes. Statistically, the models of linear regression, power-law regression and the power-law polymorphic regression are systematically tested on the basis of the statistical performance criteria in order to form physically meaningful and computationally manageable correlations. Although the Flory-Huggins and Flory-Rehner theories have been widely used to study the swelling of cross-linked polymers, the current report systematically reveals the effect of the crosslinker type and concentration on the magnitude and composition dependence of χ, which forms a thermodynamically consistent foundation of constitutive χ composition relations in transport modeling at a modest computational cost.

2. Experimental

2.1. Materials and cross-linking agents

PVA powder (86.0-89.0% hydralized, Molecular weight of 85,000-124,000), maleic acid (99.0-101%), glutaraldehyde (25% Sol) and acetic acid glacial extra pure (99.5-101%) were sourced at SD fine Chemicals. Ethanol (99.9%) was obtained from Changshu Hongsheng Fine Chemicals. A widely used cross-linking agent, namely glutaraldehyde (GA) [18,19], was selected for this study. It is a known fact that the aldehyde groups (-CHO) of glutaraldehyde may react with the hydroxyl groups (-OH) of the PVA polymer chain, which leads to the formation of a thick three-dimensional network structure. This addition can also enhance the mechanical qualities and stability of polyvinylidene (PVA), making it more applicable in specialized applications such as wound dressings, artificial organs, contact lenses, and drug delivery systems. GA is highly reactive and can be used to crosslink at temperatures down to 80 °C, allowing networks to form within minutes to hours. Maleic acid (MA) is a uronic acid and can be prepared using furfural, and it is widely applied in pharmaceuticals, surface coatings, plasticizers, oil and grease preservatives, *etc*. [18]. Food grade maleic acid is not toxic and the addition of the compound can be appropriate to improve the special fruit flavor in food and beverages, and the flavor is widely used in food additives and other areas [10].

2.2. Preparation of crosslinked PVA membranes

Poly(vinyl alcohol) (PVA) was placed in double-distilled deionized water to obtain a 10% weight polymer solution. The solution was continuously stirring at 90 °C under reflux for a minimum of 8 h to ensure complete dissolution and the creation of a homogeneous solution. The solution was left to cool to room temperature, and then the chosen agent of cross-linking was added. In the case of glutaraldehyde (GA) crosslinked membranes, the rate of concentrations of glutaraldehyde (GA) was 5 to 20 wt% to PVA with a catalytic concentration of sulfuric acid (H_2SO_4). The mixture was then left to stir for at least 24 h to achieve a homogeneous reaction and dispersing of the cross-linker. To achieve uniformly thin membranes, the casting solution was sonicated to remove trapped air and cast onto a clean glass plate utilizing a film applicator. The cast films were dried in a hot air oven at 60 °C for at least 24 h, then the membranes were peeled with great care and stored in a desiccator until further characterization. The same protocol for the preparation of membranes was applied to maleic acid cross-linked membranes without varying the polymer concentration, reaction conditions, casting, and drying parameters to allow systematic comparison.

2.3. Swelling measurements and measuring equilibrium swelling degree

The behavior of the prepared PVA membranes to swell in selected acidic and alcoholic solutions was measured. Specimen membranes of the same size and thickness were dried at 60 °C in a hot air dryer up to a constant weight. The dry mass of the individual sample membrane was determined with an analytical scale with an accuracy of 0.1 mg. The samples were then dried, followed by immersion of the dried samples in the test solvents at room temperature in closed glass containers to prevent loss of solvent. The swelling was then left to balance, which was confirmed by no longer finding any increase in membrane weight (usually 24-48 h, depending on the solvent), and periodic weight gain was measured at set intervals to determine that equilibrium swelling was reached. The swollen membranes were carefully removed from the solvent, gently blotted using filter paper to remove excess surface liquid without applying pressure, and immediately weighed to obtain the swollen weight. The swelling degree (Q) has been determined in the following manner (Equation 1).

$$Q = \frac{\text{Weight of swollen polymer} - \text{Weight of dry polymer}}{\text{Weight of dry polymer}} \quad (1)$$

Repeated measurements were made three times and the mean value obtained was reported. The swelling was then adopted to determine the Flory-Huggins interaction parameter and the network parameters of the cross-linked PVA membranes.

2.4. Determination of Flory-Huggin interaction parameter

Flory-Huggin's interaction parameter χ, in pervaporation membranes, controls the affinity of the polymer-solvent and has significant effects on the sorption, swelling and transport behavior. Equilibrium swelling measurements were used to assess the interaction of the polymer with a nonsolvent or penetrant due to the direct reflection of polymer liquid interactions. The polymer liquid interaction parameter χ was calculated in simplified form of the Flory-Huggins expression in terms of the polymer volume fraction $\boldsymbol{v}_p$ as follows [28].

$$\chi = -\frac{\ln(1-\nu_p)+\nu_p}{{\nu_p}^2} \tag{2}$$

where χ is the Flory-Huggins polymer-liquid interaction parameter, and ν_p represents the volume fraction of polymer in the swollen membrane at equilibrium. Thermodynamic compatibility between the polymer and penetrant molecules is quantitatively measured by the value of χ. When χ is low, the polymer-penetrant interactions are stronger and swelling is larger, whereas when χ is high, the interactions between polymer and the penetrant are weaker and the uptake of the solvent is lower. This simplistic form is obtained based on the Flory-Huggins lattice theory of polymer solution under equilibrium swelling conditions, with the omission of the elastic contribution of the cross-linked network of the polymer. It is under these assumptions that the interaction parameter can be directly determined by the measured polymer volume fraction and, therefore, is a convenient way of measuring the polymer-penetrant interaction in cross-linked membranes. The polymer volume fraction in the swollen membrane $\boldsymbol{v}_p$ was calculated using the measured swelling data and the known densities of the polymer and penetrant.

2.5. Correlation analysis

An empirical correlation analysis was applied to obtain quantitative correlations among the essential structural and thermodynamic parameters of the cross-linked PVA membranes. In particular, cross-linker concentration versus swelling ratio (Q), and cross-linker concentration versus interaction parameter(χ) were correlated. Furthermore, the relationship of the interaction parameter (χ) and the solvent volume fraction (ν_p) was evaluated in various solvent systems. Simple and non-linear trends in the experimental data were studied using linear, second-order, and power-law models to explain the trends. The accuracy and predictive ability of all the models were evaluated based on the coefficient of determination (R^2), root mean square error (RMSE), and mean relative deviation (MRD), providing a methodical comparison of the tool accuracy and prediction ability.

3. Results and discussion

3.1. Effect of cross-linking on equilibrium swelling degree

Figure 1a shows the degree of the change in the swelling of PVA membranes crosslinked with the varying concentration of glutaraldehyde (GA) in equilibrium acetic acid and ethanol. The behavior of a strong swelling effect that is solvent-dependent is found. The swelling ratio of acetic acid increases progressively between 1.092 at 5% GA and 1.401 at 20 %GA. This tendency indicates that in spite of the fact that GA causes chemical crosslinking in the PVA matrix, the high affinity of acetic acid to hydroxyl groups of PVA prevails in the swelling process. The rise in the concentration of GA can result in more rigid network formation; nevertheless, acetic acid is a polar protic solvent and can enter the polymer framework and result in relaxation and swelling of the chain. However, swelling in ethanol is very low (0.098-0.132) at all GA concentrations. This implies that ethanol interacts with the cross-linked PVA network minimally. The thick cross-linking net of GA profoundly limits the uptake of ethanol, indicating the improved selectivity of the membrane to solvents. This marginal increase with higher GA content could be due to microstructural heterogeneities or the free volume left behind by crosslinking. In general, GA-cross-linked PVA membranes have high resistance to swelling in ethanol and a high affinity for acetic acid and this would be of benefit to the pervaporation-based separation of organic aqueous mixtures [9].

Figure 1b shows crosslinked PVA membranes swelling with different proportions of maleic acid (MA). In contrast to GA, MA exhibits a sharp decrease in swelling with an increase in the concentration of cross-linkers, especially acetic acid. The swelling ratio in acetic acid reduces considerably, 0.691 at 5% MA to 0.419 at 10% MA, then the swelling ratio further reduces more modestly to 0.493 at 20% MA. PVA is cross-linked with maleic acid by means of esterification between the carboxylic acid functional groups of the maleic acid and the hydroxyl group of PVA to form covalent ester bonds between the chains of the polymers. Maleic acid has two reactive carboxylic groups, which allow it to serve as a bifunctional cross-linking agent and form interchain bridges to the polymer network to enhance the overall cross-link density. The created network structure suppresses the movement of the polymer chains and minimizes the free volume occupied by solvent diffusion. The low rise that was observed at the higher concentration of the MA can be explained by the excess of MA, which added more hydrophilic carboxyl groups and partially neutralized the densification effect. The swelling values in ethanol vary slightly between 0.112 and 0.173 with an increase in MA concentration. This act indicates that crosslinking with MA creates polar functionalities that are loosely connected with ethanol, but the total swelling is low compared to the acetic acid. In comparison with GA-cross-linked membranes, MA-cross-linked PVA membranes are characterized by significantly lower swelling, which implies a greater level of network compactness and reduced solvent accessibility. This indicates that MA is a good cross-linker to regulate the excessive swelling of highly polar solvents.

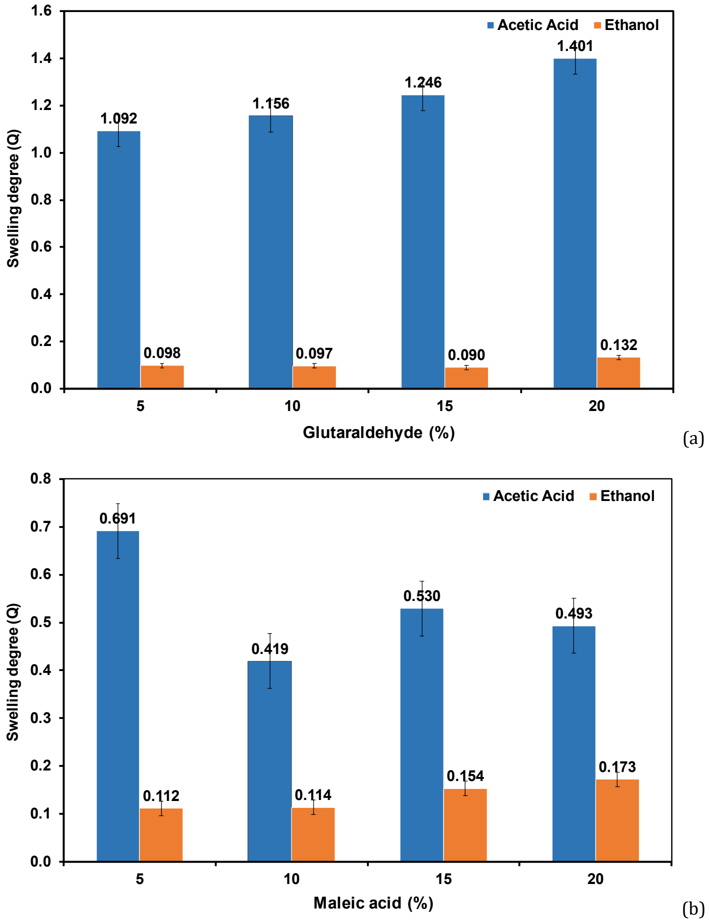
In both cross-linking systems, the maximum swelling is always greater in acetic acid than in ethanol, which supports the fact that solvent polymer interactions are the most dominant. GA-cross-linked membranes have the highest swelling in acetic acid, but MA-cross-linked membranes have the lowest total swelling, meaning that there is better control of the polymer chain motion. The corresponding statistical details are summarized in Table 1. In pervaporation, lower swelling is associated with improved dimensional stability and selectivity, whereas moderate swelling provides adequate permeability. Hence, MA-cross-linked PVA membranes would be the best to use in cases where the swelling should be controlled and the membrane should be used with high separation efficiency, whereas GA-cross-linked membranes might be beneficial in cases where high permeation flux is required.

3.2. Effect of cross-linker concentration on Flory-Huggins interaction parameter

Figure 2a illustrates how the χ changes with the concentration of maleic acid (MA) in PVA membranes in acetic acid and ethanol. In the case of acetic acid, the χ values are smaller than unity (approximately 0.83- 0.93) throughout the range of MA concentrations investigated, indicating thermodynamically positive polymer-solvent interactions. A minor increase in χ of 5 to 10% MA indicates a preliminary inhibition of the movement of polymer chains due to crosslinking by esterification.

Table 1. Quantitative comparison of equilibrium swelling behavior of cross-linked PVA membranes.

Crosslinker	Crosslinker content (%)	Solvent	Swelling degree (Q)	% Change in Q	Trend type	Crosslinker effect
GA	5 → 20	Acetic acid	1.092 → 1.401	+28.3%	Positive monotonic	Moderate
		Ethanol	0.098 → 0.132	+34.7%	Weak positive / flat	Very low (stable)
MA	5 → 20	Acetic acid	0.691 → 0.493	−28.7%	Negative monotonic	High
		Ethanol	0.112 → 0.173	+54.5%	Positive monotonic	Low



(a)

(b)

Figure 1. (a) Variation of the degree of equilibrium swelling (Q) with GA content (b) Variation of the degree of equilibrium swelling (Q) with MA content.

At sufficiently high MA concentrations, χ does not change and this shows that effective crosslinking sites are saturated. By contrast, χ values of ethanol are always above unity (1.47-1.24), confirming that there is a lack of affinity between the ethanol and the MA-cross-linked PVA membranes. The progressive reduction of χ with an increase in MA concentration could be explained by the appearance of polar carboxylic functionalities, but the reduction is not strong enough to create favorable polymer ethanol interactions. In general, MA cross-linking changes the thermodynamics of polymers and solvents largely because it increases resistance to ethanol, but the compatibility between it and acetic acid still remains reasonable.

Figure 2b represents the impact of glutaraldehyde (GA) concentration on χ. In the case of acetic acid, χ does not change significantly (0.65-0.75) with 5-20% GA, demonstrating that the polymer-solvent affinity is strong and consistent. This stability indicates that the cross-linking of GA does not alter the hydrogen-bonding interactions between PVA hydroxyl groups and acetic acid molecules significantly. In the case of ethanol, χ values of are always large (1.38-1.55), indicating thermodynamically unfavorable interactions. There is only a small reduction in χ at higher concentrations of GA, so it can be seen that network densification controls ethanol rejection most, so the polymer-solvent affinity does not change much. These findings indicate that GA-cross-linked membranes have strong thermodynamic selectivity and weak sensitivity to the cross-linker concentration with the statistical parameters and variability shown in Table 2.

3.3. Empirical correlation analysis

Linear, power-law, and polynomial regression models were used to measure the relationship between the interaction parameter (χ) and the solvent volume fraction (ν_p). Table 3 shows that all the χ-ν_p relationships have coefficients of determination greater than 99% (R^2 > 0.99), indicating that there is a strong and predictable dependence of χ on membrane composition. Figures 3a-3d show the corresponding fitting curves of linear, nonlinear, and power-law models. Polynomial regressions will give the smallest values of RMSE and MRD, which means that they will be the most statistically accurate, but it comes at an extra cost in terms of computational complexity in a transport model because it involves higher-order composition derivatives. In contrast, the power-law χ-ν_p relations provide a good compromise between precision and numerical efficiency, where R^2 values of greater than 0.99 are obtained and chemical-potential gradients in Maxwell-Stefan equations are easily evaluated.

Table 2. Quantitative comparison of the Flory-Huggins interaction parameters (χ) of cross-linked PVA membranes.

Crosslinker	Solvent	Crosslinker content (%)	Interaction parameter(χ)	% Change in χ	Trend type	Crosslinker effect
Glutaraldehyde	Acetic acid	5 → 20	0.80 → 0.90	+12	Weak nonlinear	Low
	Ethanol		1.45 → 1.25	−14	Negative monotonic	Moderate
Maleic acid	Acetic acid	5 → 20	0.75 → 0.68	−9	Nearly invariant	Very low
	Ethanol		1.55 → 1.38	−11	Weak	Low

Table 3. Statistical performance comparison of regression models.

System	Model type	Regression equation	R^2	RMSE	MRD (%)
PVA-GA + Acetic acid	Linear	$\chi = 0.4021 + 0.7272\ \nu_p$	1.000	0.00037	0.04957
	Polynomial	$\chi = 0.5589 + -0.0331\ \nu_p + 0.9187\ \nu^{2}$	1.000	0.00001	0.00122
	Power-law	$\chi = 1.0250\ \nu_p^{\,0.4270}$	0.999	0.00057	0.07609
PVA-GA + Ethanol	Linear	$\chi = -2.5140 + 4.6707\ \nu_p$	0.998	0.00390	0.22715
	Polynomial	$\chi = 16.5011 + -39.8522\ \nu_p + 26.0471\ \nu_p^{2}$	1.000	0.00016	0.00764
	Power-law	$\chi = 2.2559\ \nu^{2.7012}$	0.999	0.00320	0.18346
PVA-MA + Acetic acid	Linear	$\chi = 0.0913 + 1.3178\ \nu_p$	0.995	0.00403	0.43231
	Polynomial	$\chi = 1.0550 + -1.8334\ \nu_p + 2.5632\ \nu\boldsymbol{\nu}^{2}$	1.000	0.00031	0.02730
	Power-law	$\chi = 1.3922\ \nu^{0.8928}$	0.994	0.00422	0.44288
PVA-MA + Ethanol	Linear	$\chi = -1.6999 + 3.7068\ \nu_p$	0.998	0.00455	0.28205
	Polynomial	$\chi = 7.5338 + -18.6985\ \nu + 13.5770\ \nu_p^{2}$	1.000	0.00052	0.02916
	Power-law	$\chi = 2.0911\ \nu_p^{\,2.2510}$	0.999	0.00363	0.22826

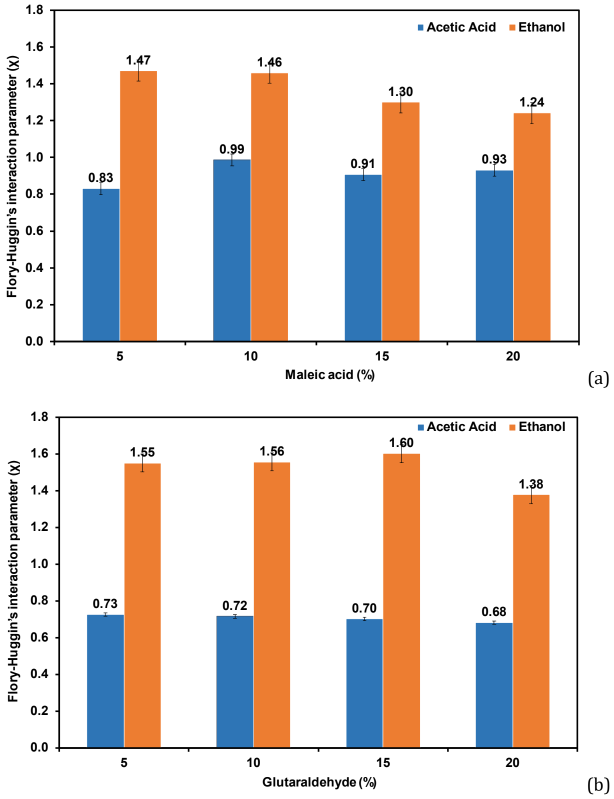


Figure 2. (a) Flory-Huggin's interaction parameter (χ) with GA content, (b) Flory-Huggin's interaction parameter (χ) with MA content.

The linear χ-ν_p approximation is the first-order dependence of the interaction parameter on the solvent volume fraction. Although this does not consider a higher-order nonlinearity in larger swelling, the resulting constant composition derivative makes it easier to calculate chemical potential gradients and could be sufficient in preliminary or reduced-order Maxwell-Stefan simulations in which detailed accuracy is not the main goal. The high goodness-of-fit of all models justifies this robustness of the experimentally-determined χ - ν_p relations and attests to the fact that the parameter of interaction is composition-dependent in nature. The suggested χ - ν_p correlations relate the thermodynamics of swelling directly to the transport driven by chemical potentials and allow the selection of model complexity wisely, depending on the requirements of accuracy and computational efficiency.

4. Conclusions

In this work, the impact of the percentage of cross-linkers on the polymer-solvent interactions in polyvinyl alcohol (PVA) pervaporation membranes was investigated systematically using the Flory-Huggins model. The interaction parameter (χ), solvent uptake, and the swelling behaviour of the membrane were measured by altering the nature of the cross-linking reagents and their concentration. The findings indicate that the crosslinking of glutaraldehyde results in stable and selective polymer–solvent interactions, which have a high affinity for acetic acid and low uptake of ethanol. In contrast, maleic acid cross-linked membranes show less swelling and more sensitivity of χ to cross-linking percentage, which is due to greater network densification by esterification.

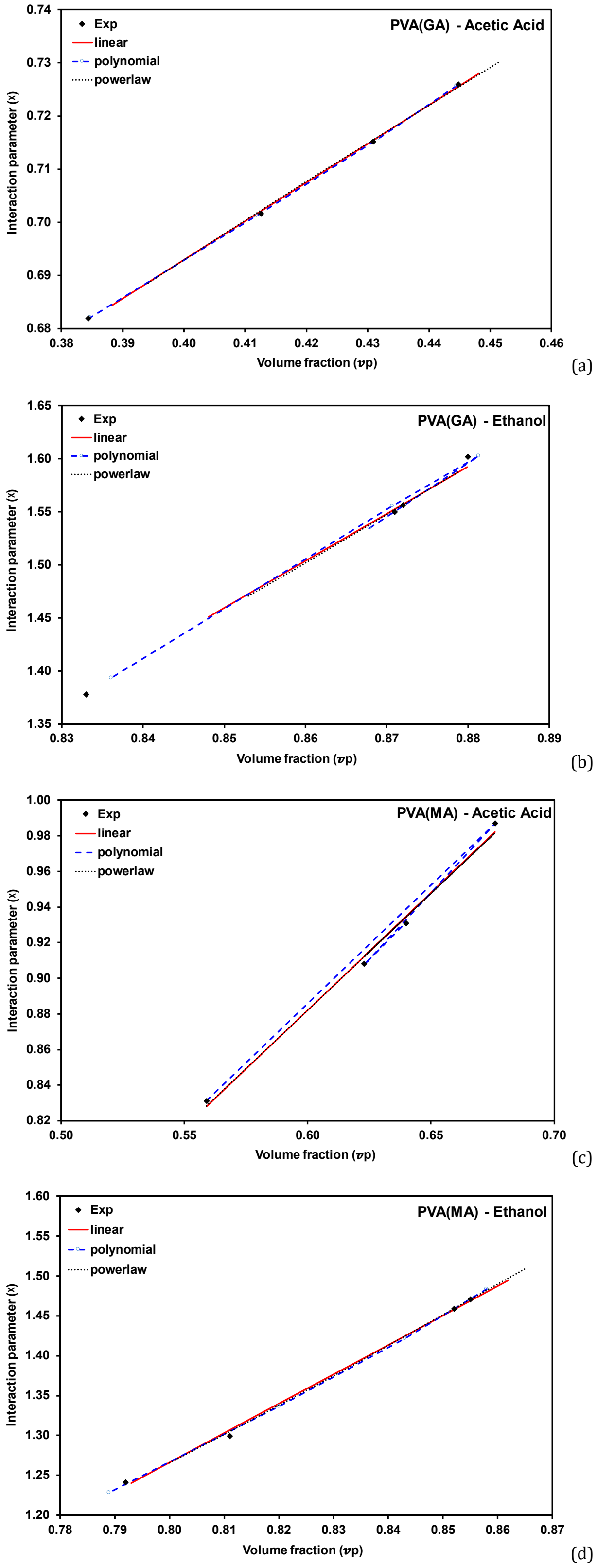


Figure 3. Regression fits for the relationship between volume fraction and interaction parameter, (a) PVA–GA (acetic acid), (b) PVA–GA (ethanol), (c) PVA–MA (acetic acid) and (d) PVA–MA (ethanol).

All membrane-solvent systems showed strong correlations between the interaction parameter (χ)and solvent volume fraction (νp) and the determination coefficients greater than 99%. These results indicate that polymer-solvent interactions within crosslinked polyvinylidene (PVA) membranes do not simply rely on the local composition and cannot be described by fixed interaction parameters. The thermodynamic description of membrane swelling using relationships obtained in this study is useful and provides a guide for the rational design of PVA-based pervaporation membranes.

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Disclosure statement

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Ethical approval: All ethical guidelines have been adhered to.

CRediT authorship contribution statement

Conceptualization: Mandavalli D. S. V. J. P. Koteswari, Suggala V. Satyanarayana ; Methodology: Mandavalli D. S. V. J. P. Koteswari, Suggala V. Satyanarayana; Software: Mandavalli D. S. V. J. P. Koteswari, Suggala V. Satyanarayana; Validation: Mandavalli D. S. V. J. P. Koteswari, Suggala V. Satyanarayana; Formal Analysis: Mandavalli D. S. V. J. P. Koteswari, Suggala V. Satyanarayana; Investigation: Mandavalli D. S. V. J. P. Koteswari, Suggala V. Satyanarayana; Resources: Mandavalli D. S. V. J. P. Koteswari, Suggala V. Satyanarayana; Data Curation: Mandavalli D. S. V. J. P. Koteswari, Suggala V. Satyanarayana; Writing - Original Draft: Mandavalli D. S. V. J. P. Koteswari, Suggala V. Satyanarayana; Writing - Review and Editing: Mandavalli D. S. V. J. P. Koteswari, Suggala V. Satyanarayana; Visualization: Mandavalli D. S. V. J. P. Koteswari, Suggala V. Satyanarayana; Funding acquisition: Mandavalli D. S. V. J. P. Koteswari, Suggala V. Satyanarayana; Supervision: Mandavalli D. S. V. J. P. Koteswari, Suggala V. Satyanarayana; Project Administration: Mandavalli D. S. V. J. P. Koteswari, Suggala V. Satyanarayana.

ORCID and Email

Mandavalli D. S. V. J. P. Koteswari
koteswarimandavalli7@gmail.com
https://orcid.org/0009-0004-7508-3741
Suggala V. Satyanarayana
svsatya7@gmail.com
https://orcid.org/0000-0001-5250-4460

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