



Understanding the Structural Changes in Nafion due to Shelf-Life and Pretreatment: Thermo Dynamical Approach of Water and Metal Ion Sorption

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ABSTRACT

Water and metal ion sorption of aged Nafion membrane have been studied. In order to understand water sorption, swelling pressure and free energy of swelling have been calculated for the water sorption data on studies carried out earlier. The larger free energy change observed on swelling of the transition metal ion form of Nafion as compared to its original protonated form indicates that hydration is more favored for the transition metal ion substituted membrane which supports its affinity toward these ions. Metal ion uptake data for differently treated aged Nafion membranes were analyzed with different isotherm models, and it is confirmed that that metal ion uptake followed chemisorption. Moreover, it was seen that pretreatment is found to affect the sorption behavior and therefore there is a change in the model that fits best to the sorption data.

Key words: Nafion membrane, Water sorption, Transition metal ion sorption, Free energy, Modeling.

1. INTRODUCTION

Membrane separation [1] finds extensive applications because of its cost effectiveness, easy operation, and high pre-concentration factor with a degree of selectivity. According to IUPAC [2], “membrane” is “a heterogeneous phase which acts as a barrier to the flow of molecules and ionic species in liquid or vapor phase.” Ion exchangers are solid polymers containing exchangeable ions, and when this is as high as 10-15 mol %, they are known as ionomers [3]. The most commonly used ionomer is a sulfonated tetrafluoroethylene based fluoropolymer-copolymer known by the trade name Nafion. These membranes have enormous applications due to their exceptional properties of thermostability, chemical inertness to corrosive conditions, good mechanical strength, permselectivity toward cation transport and easy transport of water. The property of water transport can prevent local drying that can occur in certain applications [4-6]. The properties of Nafion arises from its structure which consists clusters in the ion rich phase of the polymer and the shape and size of the clusters are affected by factors like water (solvent) content, temperature, etc., [7]. The transport within the ionomer membrane depends on the nature of ion and its mobility within the membrane phase [8-10]. Hydration of the cations plays an important role in determining the ion exchange selectivity and also affects the mobility within the membrane phase. The state of water

present has been investigated by several techniques to provide information vis-à-vis ion pair formation, ionic hydration, mobility of free water, etc., [11]. The study of water uptake is of immense significance for Nafion ionomer as it is reported that the conductivity is greatly affected by the amount of water in fuel-cell applications [12,13]. Determining and analyzing the water sorption isotherms can provide very useful information on the ion-water interactions in the resin phase. A complete understanding of ion exchange can be achieved only in terms of interactions at molecular level. The selectivity and related characteristics of the ion exchange resins based on polystyrene sulfonate cross-linked with divinyl benzene (PSS-DVB) have been fairly understood [14,15]. It is seen that the ionogenic groups (SO₃⁻) are osmotically inactive and unhydrated and therefore in the absence of strong electrostatic interactions between SO₃⁻ and the counter-ion, the resin phase behaves like single ion solutions. Nafion is expected to show ion-exchange characteristics similar to that of the gel type PSS-DVB resins. However in Nafion, there is no cross linking but the clustering of ions and water coupled with a fluorocarbon backbone can decrease the ion exchange selectivity values compared to Dowex resins. The water sorption isotherms of H⁺ and the different cationic forms of the Nafion 117, treated differently, and Dowex 50 W×4 and Dowex 50 W×8 resins have

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been generated earlier [16]. Different pretreatments were found to affect the water sorption and ion exchange properties differently due to change in the physical structure of the membrane [16].

Although a substantial amount of work has been done on water uptake by Nafion [17] literature report on the effect of water uptake on aged Nafion membrane is relatively scarce. So the free energies of swelling and swelling pressures have been calculated for the water sorption data on studies carried out earlier [16] with aged Nafion. Moreover, the water sorption data were fitted into various other models in order to gain insight into the mechanism associated with it. Earlier the ion exchange studies carried out gave the variation of the ion exchange selectivity constant with the entire range of concentration. In order to get further insight of the nature of metal ion uptake, the data [16] were analyzed with different isotherm models.

2. EXPERIMENTAL

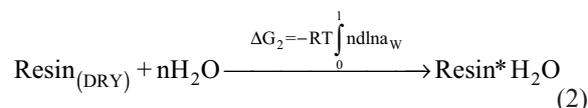
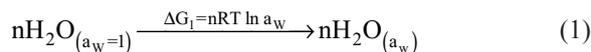
An exhaustive description of the experimental procedure has been reported in our earlier paper [16]. The determination of water sorption isotherms is carried out using isopiestic measurements, at room temperature. The ion exchange equilibrium experiments were carried out in batch mode over the entire concentration range of metal ion in solution.

3. RESULTS AND DISCUSSION

In order to understand the water and metal ion sorption in Nafion membrane, the structural aspect of ionomers is considered. Nafion structure is well known to contain different clusters and the formation of these is governed by two opposing tendencies namely the elasticity of Nafion polymer matrix and ion pair formation which depends on the ionic size of the counter ion, the degree of covalency of bond in ion pair etc. At very low concentrations of cations below the critical concentration, the formation of cluster is not favored and ion pairs are formed [18].

Thermodynamics of water sorption on Nafion membranes: The water sorption isotherms generated earlier [16] gives a correlation between the numbers of moles adsorbed as a function of water activity in the range of 0-1. The water sorption, resulting in swelling of the matrix is controlled by ion hydration and osmotic effects. The secondary solvation results in a decrease in ionic interactions to such an extent that the osmotic effects begin to predominate. However, the rigidity of the resin matrix does not allow further uptake of solvent. The water sorption isotherms indicate that at the initial water activity (low values), hydration of sulfonato group occurs but in the intermediate and higher range of water activity, hydration of ions and osmotic swelling occur respectively. In the present study, the water sorption isotherms were analyzed to obtain free energy of swelling [19]. The free energy

change can be split into two parts corresponding to the following two different equilibria and the respective free energies G_1 and G_2 are given by Equations 1 and 2.



The total free energy of water swelling is given by the sum of the free energies G_1 and G_2 .

$$\begin{aligned} \Delta G_{\text{sw}} &= \Delta G_1 + \Delta G_2 \\ &= nRT \ln a_w - RT \int_0^1 n d \ln a_w \end{aligned}$$

The amount of water adsorbed was obtained by the measurement of weight change upon equilibration in a constant isopiestic manner. These data were then fitted to a polynomial function with respect to water activity starting from the lowest non zero a_w value. Thus, the free energy values obtained were plotted versus number of moles of water sorbed, and the results are given in Figure 1.

The plot shows that ΔG_{sw} decreases sharply in the region of low value of n and begins to level off in the vicinity of a certain $n\text{H}_2\text{O}$. The initial sharp decrease in free energy could be attributed to enhancement of stability due to cationic hydration in the ion-exchanger that is followed by slight decrease due to water uptake on account of osmotic effects.

The larger free energy change observed on swelling of the transition metal ion form of Nafion as compared to its original protonated form indicates that hydration is more favored for the transition metal ion substituted

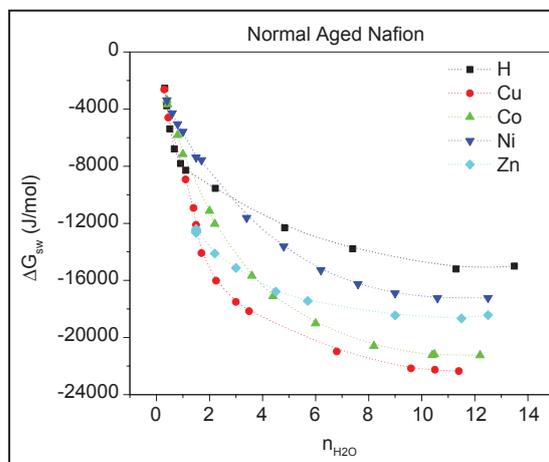


Figure 1: Plot of free energy of swelling of Nafion in different ionic forms as a function of number of moles of water sorbed.

membrane, which supports its affinity toward these ions. Enhanced hydration of transition metal ion substituted membrane can be explained from similar Lewis acidity-basicity combination of the metal ions and oxygen lone pair of the water molecule. In addition to this, the higher electro negativity of the transition metal ions as compared to proton also favors hydration in this case. The value of nH_2O where the curve levels off (n_T) can be taken to be the approximate hydration number of the cation since it indicates the maximum number of water molecules bound to the cation. The values of n_T for H, Co, Cu, Ni and Zn are 7.4, 6.03, 6.8, 9 and 9, respectively. Using these n_T values, the water activity in the swollen Nafion is obtained using Equation 4.

$$a_w = \frac{n - n_T}{n - n_T + 1} \quad (4)$$

Thus the value of water activity in the swollen membrane is then used to calculate the swelling pressure π using Equation 5, wherein \bar{V}_w is the partial molar volume of water and \bar{a}_w is the water activity in the membrane phase.

$$\pi \bar{V}_w = -RT \ln \bar{a}_w \quad (5)$$

The swelling pressures calculated for the different forms of Nafion membrane is given in Figure 2.

The variation in swelling pressure of H form with that reported in the literature [20] is within 6%. The increasing order of swelling pressure matches the selectivity order as reported in [16]. It is concluded that the larger is the swelling pressure difference between protonated form and the metal ion form, the lesser is the selectivity toward ion-exchange.

The water sorption isotherms of the different forms of Nafion were fitted into the modified Park's dual mode adsorption model [21] as described by the Equation 6, wherein n_w denotes the moles of water adsorption per gram equivalent of Nafion, a_w is the water activity, A the Langmuir capacity constant, b_L Langmuir affinity constant, K_c the equilibrium constant for clustering reaction and n the mean number of water molecules per cluster.

$$n_w = \frac{Ab_L a_w}{1 + b_L a_w} + \frac{K_c s^n a_w^n}{n} \quad (6)$$

From the fitting, the protonated and the Cu forms showed reasonably low deviation from the experimental data (Figure 3). It may be noted that the fitting is good only for low water activity values. This indicates that probably very well-defined water clusters are not formed in aged Nafion, which has lost a part of its elasticity.

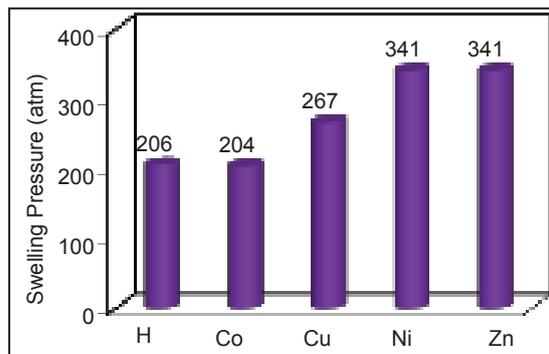


Figure 2: Plot of swelling pressure of Nafion for different ionic forms.

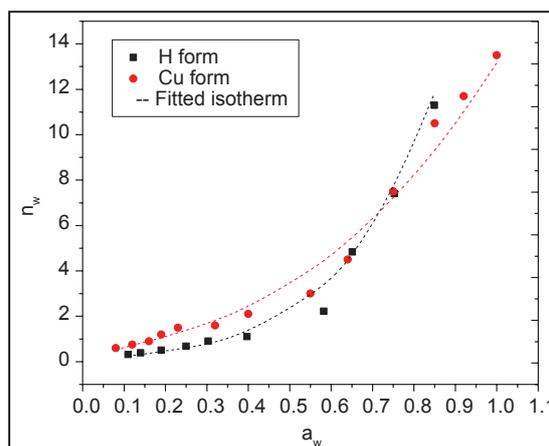


Figure 3: Plot of number of moles of water sorbed as a function of water activity as fitted to Park's Dual mode model.

3.1. Equilibrium Modeling of Metal Ion Sorption

The ion exchange isotherms are the plots of equivalent fractions of the metal ions in the resin phase q_e (mmoles/g) versus those in solution C_e (mmoles/L). The metal sorption data were fitted to the various equilibrium adsorption models. Langmuir can be used to compare the sorption efficiency of various sorbents. The assumptions of this model are that adsorption is monolayer and occurs at finite defined localized identical and equivalent sites with no hindrance from each other. The mathematical expressions of Langmuir isotherm in non-linear and linear forms are given in Equation 7 (a) and (b) respectively.

$$q_e = \frac{Q^0 * b * C_e}{1 + b * C_e} \quad (7a)$$

$$\frac{C_e}{q_e} = \frac{1}{Q^0 * b} + \frac{C_e}{Q^0} \quad (7b)$$

The Freundlich isotherm describes the non-ideal and reversible adsorption and can be applied to multilayer adsorption and the mathematical expressions (non-linear and linear respectively) given in Equation 8(a) and 8(b) respectively can be used to

understand the surface heterogeneity and nature of sorption.

$$q_e = K_f * C_e^{1/n} \quad (8a)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (8b)$$

The Dubinin–Radushkevich (D–R) isotherm is an empirical model initially conceived for the adsorption of subcritical vapors onto micro porous solids following a pore–filling mechanism. This model is often successful for high and intermediate concentration ranges but deviates at lower concentration. This has been used to distinguish the physical and chemical adsorption of metal ions. The model expressed by Equation 9 gives the correlation between the Polanyi potential ϵ ($=RT \ln(1+1/C_e)$) and the amount sorbed. The slope of the plot, β , is the degree of heterogeneity ($0 < \beta < 1$) and can be used to calculate the energy of sorption E_s using Equation 10.

$$\ln q_e = -\beta \epsilon^2 + \ln Q \quad (9)$$

$$E_s = \frac{1}{\sqrt{2 \times \beta}} \quad (10)$$

Temkin isotherm model was applied to evaluate the adsorption potentials of adsorbents for adsorbates, i.e., metal ions from aqueous solution. The model is expressed by Equation 11, where A_T (L mg⁻¹) is the Temkin equilibrium binding constant, and b (dimensionless) is the Temkin isotherm constant.

$$q_e = \frac{RT}{b} \ln A_T + \frac{RT}{b} \ln C_e \quad (11)$$

Out of these four 2-parameter isotherm models (Langmuir, Temkin, Freundlich and D–R) D–R is the only model that deals with adsorption on heterogeneous surfaces. These four equations have been plotted in linear form for its obvious simplicity. Other non-linear 3-parameter models which deal with heterogeneity are sips, toth and Redlich-Peterson (RP) adsorption models. Non-linear optimization provides a more complex, but mathematically rigorous method for determining isotherm parameter values. So we have also fitted our adsorption data to the three non-linear isotherm models, namely sips, toth and RP. RP model (Equation 12) combines models of Freundlich and Langmuir and describes the heterogeneity of sorbent surface containing a certain number of adsorption sites with the same adsorption potential. The equation by RP is the following:

$$q_e = \frac{K_R C_e}{1 + a_R * C_e^R} \quad (12)$$

Sips isotherm, a combination of Langmuir and Freundlich, can be used for predicting the heterogeneous adsorption systems. At low adsorbate concentrations, it reduces to Freundlich isotherm, while at higher concentrations it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm. The relationship is given by Equation 13.

$$q_e = \frac{K_S * C_e^{\beta_s}}{1 + a_s * C_e^{\beta_s}} \quad (13)$$

Toth isotherm model is an empirical equation to improve Langmuir isotherm and used for describing heterogeneous adsorption systems at low and high concentration. Its correlation assumes an asymmetrical quasi-Gaussian energy distribution.

$$q_e = \frac{K_T * C_e}{(C_e + a_T)^{1/t}} \quad (14)$$

Figure 4 gives an overall idea of the various models that were used and the extent to which each metal ion sorption could be fitted to these models.

It is seen that the pretreatment has an effect on the sorption behavior and therefore there is a change in the model that fits best. From Figure 4a, it is seen that for normal aged Nafion, the sorption of Cu does not follow Freundlich while in the water pretreated Nafion only Freundlich is applicable. In acid pretreated Nafion sorption of Cu does not conform to any of the 2-parameter models. For normal aged Nafion, the cobalt sorption does not follow any of the four models whereas in acid pretreated, the sorption follows Freundlich and D–R models while the water pretreated Nafion follows both the Langmuir and Temkin models. The nickel ion sorption in normal aged Nafion does not obey any of the 2-parameter models. It conforms to Langmuir and Freundlich for water pretreated Nafion and to temkin and D–R models for acid treated Nafion. The zinc sorption in normal aged Nafion follows all the models except D–R. D–R model is obeyed by Zn sorption in acid pretreated Nafion while, for the sorption with water pretreated aged membrane, none of the models seem to be applicable. The values of uptake studies showed that the maximum capacity values of CuN, CoWT, NiWT and ZnN were 1.177, 1.678, 1.273 and 1.668 mM/g. The fitting from D–R model confirms that the sorption is the chemisorption, and this is in accordance with the results of Freundlich model. Figure 4b gives an idea of the fitting with the non-linear forms of the various models and the goodness of fit obtained with these non-linear models is shown in Tables 1-3.

4. CONCLUSIONS

The larger free energy change observed on swelling of the transition metal ion form of Nafion as compared to its original protonated form indicates that hydration is

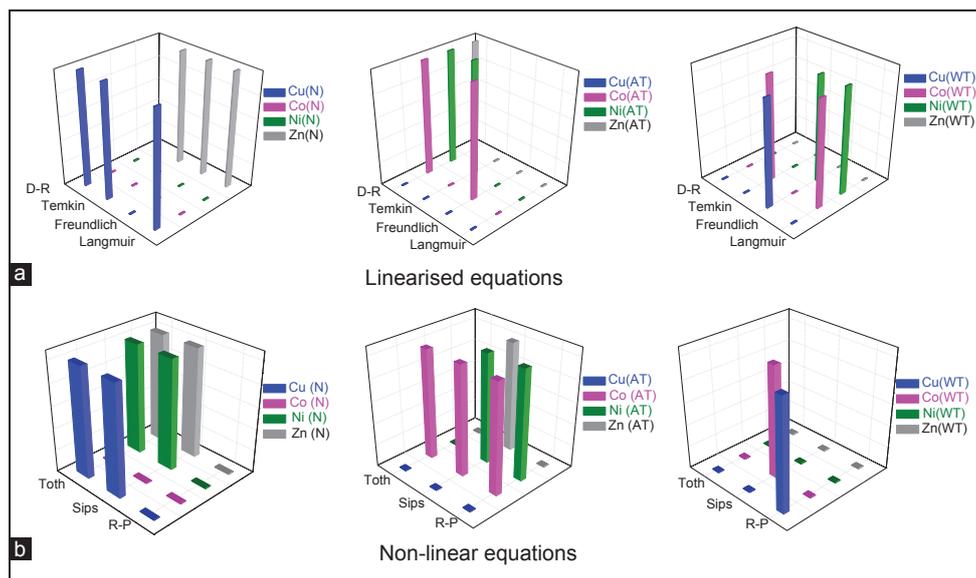


Figure 4: Representation of various models of metal ion sorption using, (a) Linear forms of Langmuir, Freundlich, Dubinin–Radushkevich and Temkin; (b) non-linear forms of the equations of sips, toth, and Redlich-Peterson models.

Table 1: Non-linear fit parameters for RP model (correlation to highest R^2 value).

Metal ion	R^2	K_R (L/g)	a_R (L/mmol)	β_R
CuWT	0.994	4.305	3.47	0.267
CoAT	0.994	2.779	1.75	0.847
NiAT	0.996	2.043	1.228	1.572
ZnN	0.996	2.703	1.659	0.803

RP=Redlich-Peterson

Table 2: Non-linear fit parameters for Sips model (correlation to highest R^2 value).

Metal ion	R^2	K_S (L/g)	β_S	a_S (L/mmol)
CuN	0.993	2.755	0.789	1.891
CoWT	0.996	4.748	1.504	4.148
CoAT	0.994	2.155	0.932	1.149
NiAT	0.996	4.741	1.336	4.06
NiN	0.993	2.356	0.998	1.349
ZnN	0.997	2.057	0.937	1.042
ZnAT	0.996	1.764	1.01	0.676

Table 3: Non-linear fit parameters for toth model (correlation to highest R^2 value).

Metal ion	R^2	K_T (mmol/g)	A_T (mmol/L)	$1/t$
CuN	0.994	1.038	0.106	0.756
CoAT	0.994	1.234	0.328	0.695
NiN	0.993	1.385	0.483	0.788
ZnN	0.998	1.183	0.273	0.606

more favored for the transition metal ion substituted membrane which supports its affinity toward these ions. The increasing order of swelling pressure matches the selectivity order as reported. This indicates that probably very well-defined water clusters are not formed in aged Nafion, which has lost a part of its elasticity. The values of uptake studies showed that the maximum capacity values of CuN, CoWT, NiWT and ZnN were 1.177, 1.678, 1.273 and 1.668 mM/g. The fitting from D–R model confirms that the sorption is the chemisorption, and this is in accordance with the results of Freundlich model. It is seen that the pretreatment has an effect on the sorption behavior and therefore there is a change in the model that fits best.

5. REFERENCES

1. K. Pabby, S. S. H. Rizvi, A. M. Sastre Requena. (Eds.), (2008) *Handbook of Membrane Separations: Chemical, Pharmaceutical, Food, and Biotechnological Applications*, Boca Raton: Taylor & Francis, CRC Press.
2. W. J. Koros, Y. H. Ma, T. Shimadzu, (1996) Terminology for membranes and membrane processes (IUPAC Recommendations 1996). *Pure and Applied Chemistr*, **68**: 1479-1489.
3. M. Pineri, A. Eisenberg, (Eds.), (2012) *Structure and Properties of Ionomers*, Netherlands: Reidel Publishing Company.
4. J. W. Weidner, M. Doyle, (2000) Report on the electrolytic industries for the year 1999, *Journal of the Electrochemical Society*, **147**: 3953.
5. S. Banerjee, D. E. Curtin, (2004) Nafion® perfluorinated membranes in fuel cells, *Journal of Fluorine Chemistry*, **125**: 1211.
6. M. A. Harmer, W. E. Farneth, Q. Sun, (1996) High

- surface area Nafion resin/silica nanocomposites: A new class of solid acid catalyst, *Journal of the American Chemical Society*, 118: 7708.
7. A. Eisenberg, B. Hind, R. B. Moore, (1990) A new multiplet-cluster model for the morphology of random ionomers, *Macromolecules*, 23: 4098.
 8. N. Grossi, E. Espuche, M. Escoubes, (2001) Transport properties of Nafion (R)/cyclodextrin membranes, *Separation And Purification Technology*, 22/23: 255.
 9. S. Koter, (2001) Transport number of counterions in ion-exchange membranes, *Separation And Purification Technology*, 22/23: 643.
 10. I. Cabasso, Z. Z. Liu, and T. Mackenzie J, (1986) The permselectivity of ion-exchange of alcohol/water mixtures with nafion membranes, *Journal of Membrane Science*, 28: 109.
 11. D. A. White, and R. L. Bussey, (1997) Water sorption properties of modified clinoptilolite, *Separation and Purification Technology*, 11: 137.
 12. T. E. Springer, T. A. Zawodzinski Jr, S. Gottesfeld, (1991) Polymer electrolyte fuel cell model, *Journal of The Electrochemical Society*, 138: 2363.
 13. T. A. Zawodzinski Jr., M. Numan, L. Silberud, S. Gottesfeld, (1991) Determination of water diffusion coefficients in perfluorosulfonate ionomeric membranes, *Journal of Physical Chemistry*, 95: 6040.
 14. A. R. Gupta, (1991) Molecular level interpretation of ion exchange selectivity, *Indian Journal of Chemistry*, 29A: 409.
 15. S. T. Iyer, D. Nandan, R. M. Iyer, (1992) Thermodynamic equilibrium constant of alkali metal ion-proton and related swelling free energy in perfluoro-sulphonate ionomer (Nafion 117) membrane, *Indian Journal of Chemistry*, 31A: 317.
 16. J. Ramkumar, T. Mukherjee, (2007) Effect of aging on the water sorption and ion exchange studies on Nafion and Dowex resins: Transition metal ions-proton exchange systems, *Separation and Purification Technology*, 54: 61.
 17. J. Ramkumar, (2012) Nafion perfluorosulphonate membrane: Unique properties and various applications. In S. Banerjee, A. K. Tyagi, (Eds.), *Functional Materials*, Oxford, U.K: Elsevier Inc.
 18. H. K. Pan, A. Meaghar, M. Pineri, G. S. Knapp, S. L. Cooper, (1985) EXAFS studies of Fe³⁺ + neutralized Nafion: Interpretation of the second peak in the radial structure function, *The Journal of Chemical Physics*, 82: 1529.
 19. F. Helfferich, (1962) *Ion Exchange*, New York: McGraw Hill Book Co.
 20. K. K. Pushpa, D. Nandan, R. M. Iyer, (1988) Thermodynamics of water sorption by 50 W ion-exchange resins at 298 +/- 1-K, *Journal of the Chemical Society Faraday Transactions*, 184: 2047.
 21. G. S. Park, (1986) Transport principles-solution, diffusion and permeation in polymer membranes. In P. M. Bungary, (Ed.), *Synthetic Membranes: Science, Engineering and Applications*, Holland: Reidel.

*Bibliographical Sketch



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