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Thermodynamics of Hydrogen Bonding in Solutions of Poly(vinylpyrrolidone) in Ethanol/CCl_4 Mixtures

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ABSTRACT: The Gibbs free energy, the enthalpy, and the entropy of mixing of ethanol with the polymer poly(vinylpyrrolidone) (PVP) and with its low molecular weight analog, *N*-ethylpyrrolidone (NEP) were calculated. The calculation of the free energy of mixing was achieved with the thermodynamic model for hydrogen-bonded polymer systems developed by Painter, Coleman, and Graf. This model, based on the use of an association model, gives the free energy of mixing as a function of the Flory−Huggins interaction parameter, the composition of the mixture, and the association equilibrium constants. The self-association of the ethanol molecules was described by two equilibrium constants, one for the formation of dimers and one for the formation of multimers. The equilibrium constants of interassociation of PVP or NEP with ethanol were determined from the quantitative analysis of NEP/ethanol and PVP/ethanol FTIR spectra at various temperatures and compositions. The values of the equilibrium constants were then used to calculate the theoretical Gibbs free energy of mixing as a function of the composition. The enthalpic and entropic contributions to mixing were compared for the NEP/ethanol and PVP/ethanol mixtures.

Introduction

Water-soluble polymers are used in a variety of applications including colloid dispersants, adhesives, and, more recently, as interphase modifying agents for fiber-reinforced composites. An understanding of the thermodynamics of polymer−solvent interactions is essential, particularly when modeling the adsorption of polymers onto solid surfaces from solution.[1]

In general, polymer adsorption is reduced as the polymer−solvent interaction becomes more favorable, i.e., with decreasing value of the Flory−Huggins χ parameter. This is well known experimentally[1] and can be explained by self-consistent field theories for polymer adsorption.[1−5] The dimensionless segmental adsorption energy for a polymer adsorbing on a surface from a solvent, χ_s^{po}, is the change in energy when a polymer segment breaks certain contacts with solvent molecules, adsorbs onto a surface, and displaces some solvent molecules.[6] Cohen Stuart et al. developed a displacement technique for measuring χ_s using a lattice model.[2,3] It was shown that χ_s depends upon χ as well as a critical segmental adsorption energy term χ_{sc} and a critical displacer volume fraction ϕ_{cr}. Using the displacement technique, it was shown that $\chi_s kT$ for poly(vinylpyrrolidone) (PVP), the polymer used in the present study, was approximately $4kT$ when adsorbing onto silica from water and from dioxane.[3] Specific polymer−solvent interactions can be important as was shown by Chen et al., who measured values of $\chi_s kT$ for poly(2-ethyl-2-oxazoline) to be $5kT$ and $3kT$ when adsorbing onto silica from water and from ethanol, respectively.[7]

One problem with modeling the adsorption of polymers that exhibit strong hydrogen-bonding interactions with solvents has been the difficulty of incorporating these specific interactions into a self-consistent field theory. Most adsorption theories use the Flory−Huggins theory, which ignores specific interactions, to account for polymer−solvent interactions. The approach by Ploehn et al. is useful in this regard because the polymer−solvent interactions are accounted for in the form of an equation of state.[4,5] The effect of polymer−solvent hydrogen-bonding interactions on adsorption can, in principle, be incorporated by using an equation of state that accounts for hydrogen bonding. On the other hand, Coleman et al. modified the Flory−Huggins theory by adding a free energy term for hydrogen bonding to the expression for the total free energy of mixing.[8−10] In this model, the free energy of mixing is a function of the self-association and interassociation equilibrium constants, the Flory−Huggins interaction parameter, the composition of the mixture, and specific molecular characteristics of the components of the mixture. The predictive capabilities of this model have already been tested on polymer blends containing poly(vinylphenol)[11−15] or vinyl alcohols[16,17] as the self-associating components and poly(vinyl acetate) or poly(methacrylic acids) as the interassociating components. The model has also been tested on blends containing ether and phenoxy groups.[18−20] It appears to successfully predict the phase diagrams of these polymers blends.

The purpose of the present work is to use the approach of Coleman et al. to quantify the free energy of mixing of the polymer PVP and its low molecular weight analog *N*-ethylpyrrolidone (NEP) with ethanol. Ethanol is a polar solvent which self-associates. Fourier transform infrared spectroscopy was employed to determine the hydrogen-bonding equilibrium constants.

Background

The model developed by Coleman, Graf, and Painter describes the Gibbs free energy of mixing two components A and B that undergo specific interactions by the following equation:[8−10,21,22]

$$\frac{\Delta G_m}{RT} = \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \chi_B + \chi \phi_A \phi_B + \frac{\Delta G_H}{RT} \quad (1)$$

where ϕ_i is the volume fraction of the component i, N_i is the degree of polymerization, χ is the interaction parameter, and the ΔG_H term takes into account the specific interactions favorable for mixing, most commonly hydrogen bonds. In a binary mixture where B

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self-associates while A can form hydrogen bonds only with B and where the self-association is described by two equilibrium constants, the equilibrium constants are defined as

$$B_h + A_1 \overset{K_A}{\longleftrightarrow} B_hA \qquad \text{with} \qquad K_A = \frac{\phi_{BhA}}{\phi_{Bh}\phi_{A1}}\frac{hr}{h+r} \tag{2}$$

$$B_1 + B_1 \overset{K_2}{\longleftrightarrow} B_2 \qquad \text{with} \qquad K_2 = \frac{\phi_{B2}}{2\phi_{B1}^2} \tag{3}$$

$$B_1 + B_h \overset{K_B}{\longleftrightarrow} B_{h+1}\ (h > 1) \qquad \text{with} \qquad K_B = \frac{\phi_{Bh+1}}{\phi_{Bh}\phi_{B1}}\frac{h}{h+1} \tag{4}$$

where the variable r represents the ratio of the molar volumes of the A and the B units. In our study, the terms A_1 and B_1 will represent the polymer repeat unit and the polar solvent molecule, respectively, and B_h and B_{h+1} represent the associated solvent complexes containing h and $h + 1$ solvent molecules, respectively.

The total volume fraction of all A and B units, ϕ_A and ϕ_B, is given by

$$\phi_A = \phi_{A1} + K_A\phi_{A1}\phi_{B1}\Gamma_1 \tag{5}$$

$$\phi_B = \phi_{B1}\Gamma_2\left[1 + \frac{K_A\phi_{A1}}{r}\right] \tag{6}$$

where the functions Γ_1 and Γ_2 are defined as

$$\Gamma_1 = \left(1 - \frac{K_2}{K_B}\right) + \frac{K_2}{K_B}(1 - K_B\phi_{B1})^{-1} \tag{7}$$

$$\Gamma_2 = \left(1 - \frac{K_2}{K_B}\right) + \frac{K_2}{K_B}(1 - K_B\phi_{B1})^{-2} \tag{8}$$

In these equations, K_2 and K_B are the self-association equilibrium constants and K_A is the interassociation equilibrium constant. K_2 describes the formation of dimers whereas K_B describes the formation of multimers. Following Flory's lattice theory,[23] Coleman et al. developed an expression for ΔG_H:

$$\frac{\Delta G_H}{RT} = \phi_B \ln\left[\frac{\phi_{B1}}{\phi_{B1}^0\ \phi_B^{1/n\mathrm{H}-0}}\right] + \frac{\phi_A}{R}\ln\left[\frac{\phi_{A1}}{\phi_A}\right] + \phi_B\left[\left(\frac{{\Gamma_1}^0}{{\Gamma_2}^0}\right) - \left(\frac{\Gamma_1}{\Gamma_2}\right)\right] + \phi_B\left(\frac{\Gamma_1}{\Gamma_2}\right)\left[\frac{X}{1+X}\right] \tag{9}$$

where the function X is defined as $X = K_A\ \phi_{A1}/r$ and $\bar{n}_H^0$ is the number-average length of the hydrogen-bonded chains in a solution of pure B.

$$1/\bar{n}_H^0 = {\Gamma_1}^0/{\Gamma_2}^0 \tag{10}$$

In eqs 9 and 10, the superscript "0" refers to the solution of pure B units. The advantage of this theory is that all these parameters can be determined by independent experimental measurements.

Experimental Section

Spectrophotometric grade ethanol was purchased from AAPER Alcohol and Chemical Co. and spectrophotometric grade carbon tetrachloride from Fisher Scientific. They were used without further purification. The purity, or more precisely, the dryness of ethanol was verified by infrared spectroscopic measurements before use. This was achieved by recording the infrared spectra of ethanol/water mixtures at various compositions. A water peak appeared around 3680 cm^{-1} for water content above 0.5% by volume in ethanol. The absence of a water peak in our mixtures shows that the water content in ethanol was lower than 0.5%. Poly(vinylpyrrolidone) (PVP) of grade 12 PF was purchased form BASF under the name Kollidon. The grade 12 PF corresponds to a number-average molecular weight equal to 1300 g mol^{-1} or a degree of polymerization of 12. The PVP was dried before use in an oven at 120 °C for 24 h. *N*-Ethylpyrrolidone (NEP) was purchased from Fisher Scientific. Accurate dilution of the NEP/ethanol and PVP/ethanol mixtures in CCl_4 was performed using Labsystem micropipettes. In the ternary mixtures, the concentration of NEP and PVP repeat units was set to 0.04 mol L^{-1}. The concentration of ethanol was then adjusted in terms of molar fractions relative to the molar concentration of NEP monomers or PVP repeat units. The NEP/ethanol/CCl_4 mixtures were stirred 1 h before use whereas the PVP/ethanol/CCl_4 mixtures were stirred 12 h to ensure complete mixing. Since PVP is not soluble in CCl_4, the concentration of ethanol had to be high enough in the ternary mixtures to ensure total solubility of PVP. The minimum molar fraction of ethanol needed to ensure total solubility of PVP was found to be 80 mol of ethanol to 20 mol of PVP repeat units.

Infrared spectra were collected with a BIO-RAD FTS 40A spectrometer with a MCTA detector at a resolution of 2 cm^{-1}. The samples were contained in a demountable precision liquid cell purchased from Harrick Scientific Corp. with two KBr windows and a 0.25 mm thickness spacer. The temperature of the sample was measured with a thermocouple and regulated at ±0.1 °C with an OMEGA CN-2011 programmable controller. Each spectrum contained 64 signal-averaged scans. In the case of temperature studies, the absence of degradation or leaks in the cell was verified by monitoring the area of the band around 2950 cm^{-1} associated with the symmetric and asymmetric CH stretching vibration of the ethanol aliphatic CH_2 groups, which is a noninteracting band, as a function of temperature.[8] The area of this band remained constant. The curve-fitting of the hydroxyl and carbonyl stretching bands was achieved using a spectrum analysis program, Grams/386, from Galactic Industries Corp. The curve-fitting results were validated by the consistency in the variations of frequencies, widths at half-height, and areas with temperature and ethanol concentration[2] (see Tables 1 and 2). The energy of mixing curves were calculated using the Miscibility Guide and Phase Calculator Software, MG&PC, written by Coleman et al.[8] This program computes both the expression of the total volume fraction of all A and B units given in eqs 5 and 6 and the expression of the Gibbs free energy for a binary mixture with specific interactions given in eqs 1 and 9.

Results and Discussion

The free energy, the enthalpy, and the entropy of mixing PVP with ethanol were determined and compared with values obtained for the low molecular weight analogue NEP in ethanol. In these mixtures, the ethanol molecules are the self-associating B units while the PVP repeat units or the NEP molecules are the interassociating A units. In order to calculate the Gibbs free energy of mixing using the expression developed by Coleman et al., the interaction parameters and the equilibrium constants of hydrogen bond formation had to be determined independently.

Determination of the Interaction Parameter. In the expression of the Gibbs free energy of mixing, eq 1, the parameter χ accounts only for the physical interactions which include the dispersive and weak polar forces. The value of χ is thus the same as the one used in the Flory−Huggins expression of the Gibbs free energy of mixing for regular solutions. The interaction parameter can be estimated using the solubility param-

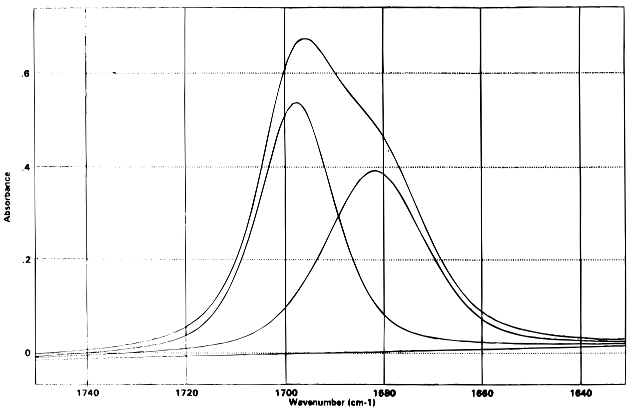

Figure 1. FTIR spectra in the carbonyl region of a 20/80 molar ratio NEP/ethanol mixture, diluted in CCl_4, at a temperature of 50 °C.

eters, δ, introduced by Hildebrand and Scott:[24]

$$\chi = \frac{V_R}{RT}[\delta_A - \delta_B]^2 \tag{11}$$

where δ_i is the solubility parameter of the component i and V_R is the reference volume, usually taken as the molar volume of the specific repeat unit of the self-associating component. Using the group contribution method,[25−27] the NEP solubility parameter was found to be equal to 21.5 $(J/cm^3)^{1/2}$. The ethanol solubility parameter is 26.0 $(J/cm^3)^{1/2}$.[25] The solubility parameter for PVP was calculated using the group contribution method and compared to the values found in the literature.[28−30] Summarizing these results, its value ranged from 25.6 to 26.2 $(J/cm^3)^{1/2}$. We used the value determined by the experimental method,[28] namely 25.6 $(J/cm^3)^{1/2}$.

Determination of the Self-Association Equilibrium Constants. The self-associating equilibrium constants were determined from the quantitative analysis of the infrared spectra of ethanol diluted in CCl_4 at various concentrations and temperatures.[31] Since the absorption coefficients of the bands associated with the stretching of the free and non-hydrogen-bonded hydroxyl groups depend on both the temperature and the strength of the hydrogen-bonding interaction, we could not use the hydroxyl band in direct quantitative analysis of the spectra. Instead, the equilibrium constants were determined using a method developed by Coggeshall and Saier[32] where the extinction coefficient of the the band associated with the free hydroxyl groups is determined by extropolating absorption data to zero ethanol concentration. At $T = 25$ °C, the equilibrium constants were found to be $K_2 = 1.08$ L mol^{-1} in terms of molar concentrations or 18.4 in terms of molar fractions and $K_B = 3.52$ L mol^{-1} in terms of molar concentrations or 60.0 in terms of molar fractions.[31] The enthalpy of dimerization for ethanol was found to be −4.61 kcal mol^{-1} and the enthalpy for multimer formation was found to be −4.15 kcal mol^{-1}. These values were determined for ethanol concentrations ranging from 0.19 to 0.76 mol l^{-1}.

The Carbonyl Band. The infrared spectra of NEP/ethanol and PVP/ethanol mixtures diluted in CCl_4 were measured at temperatures varying from 40 to 65 °C and ethanol concentrations varying from 0.06 to 0.76 M for NEP mixtures and from 0.18 to 0.76 M for PVP mixtures. Figure 1 presents the carbonyl stretching region of a NEP/ethanol mixture. This region, ranging from 1630 to 1750 cm^{-1}, consists of two contributing bands. The first band, around 1698 cm^{-1}, is due to the stretching of the nonhydrogen-bonded or free groups. The second band, around 1680 cm^{-1}, is due to the stretching of the hydrogen-bonded groups. The interassociation equilibrium constant, K_A, can be obtained by analyzing the effect of varying the temperature and the ethanol concentration on the carbonyl band. First, the ratio of the absorptivity coefficients of the carbonyl band needs to be determined in order to calculate the fraction of hydrogen-bonded carbonyl groups from the quantitative analysis of any mixture spectrum. Tables 1 and 2 present the results of the curve-fitting of the carbonyl band for NEP and PVP mixtures, respectively. For PVP/ethanol mixtures as well as for NEP/ethanol mixtures, the bands associated with the free and the hydrogen-bonded carbonyl groups shift to higher frequencies when the temperature increases from 40 to 65 °C. Similar shifts to higher frequencies of the hydrogen-bonded band are observed when the ethanol concentration decreases. These shifts, on the order of 2 cm^{-1}, are resulting from the decrease of the average strength of the hydrogen bonds. Tables 1 and 2 also show that when the temperature increases or when the ethanol concentration decreases, the area of the free carbonyl stretching band increases, whereas the area of the hydrogen-bonded band decreases. A decrease of the total area of the carbonyl bands with increasing temperature was also observed. This decrease is due to the difference in the absorptivity coefficients of both bands.

Determination of the Ratio of the Absorptivity Coefficients. Two bands appear in the carbonyl stretching region, one associated with the stretching of the free carbonyl groups and another one associated with the hydrogen-bonded carbonyl groups. At any temperature or ethanol concentration, the Beer−Lambert law can written as

$$c_T = c_{HB} + c_F = \frac{(A_{HB})_T}{ba_{HB}} + \frac{(A_F)_T}{ba_F} = \frac{(A_{HB})_{COH}}{ba_{HB}} + \frac{(A_F)_{COH}}{ba_F} \tag{12}$$

where c_T is the total concentration of carbonyl groups, c_{HB} is the concentration of hydrogen-bonded groups, c_F is the concentration of free carbonyl groups, b is the thickness of the sample, a_{HB} is the absorptivity coefficient of the hydrogen-bonded band, a_F is the absorptivity coefficient of the free band, $(A_F)_T$ is the area of the free carbonyl band at a given T temperature, and $(A_F)_{COH}$ is the area of the free carbonyl band at a given total concentration of hydroxyl groups, COH. If the absorptivity coefficients are independent of temperature and ethanol concentration, all the points are scattered around the line given by

$$(A_{HB})_{COH} + \alpha(A_F)_{COH} = \text{constant} \quad \text{or} \quad (A_{HB})_T + \alpha(A_F)_T = \text{constant} \tag{13}$$

where α is the ratio of the absorptivity coefficients, defined as a_{HB}/a_F. The ratio of the absorptivity coefficients can be experimentally determined by analyzing the FTIR spectra of mixtures obtained at different ethanol concentrations and at temperatures ranging from 40 to 65 °C. Figures 2 and 3 present the plots of the area of the band associated with the hydrogen-bonded groups versus the area of the band associated with the free groups for NEP and PVP mixtures, respectively. At a given ethanol concentration, the

Table 1. Curve-Fitting Results of NEP/Ethanol Mixtures Diluted in CCl_4

T (°C)	free center (cm^{-1})	C=O width (cm^{-1})	band area	HB[a] center (cm^{-1})	C=O width (cm^{-1})	band area	$f_F^{C=O}$ [b]
5/95[c]							
45	1697.41	14.99	2.43	1677.98	30.27	26.42	0.115
50	1697.75	15.37	2.61	1678.54	30.19	26.00	0.125
55	1698.23	15.22	2.59	1679.14	30.6	25.28	0.127
60	1698.57	15.44	2.76	1679.69	30.56	24.99	0.135
65	1698.97	15.56	2.93	1680.32	30.52	24.82	0.144
8/92							
40	1696.55	16.46	3.94	1678.34	28.67	22.24	0.201
45	1696.17	16.83	4.52	1679.22	28.62	21.17	0.232
50	1697.57	16.93	4.94	1679.81	28.54	20.56	0.254
55	1697.92	16.95	5.19	1680.35	28.51	20.04	0.269
60	1698.28	16.99	5.57	1680.92	28.43	19.45	0.289
65	1698.66	16.99	5.91	1681.54	28.39	18.90	0.308
10/90							
40	1696.72	17.47	6.47	1679.05	27.29	19.42	0.321
45	1697.20	17.54	6.94	1679.75	27.25	18.76	0.344
50	1697.51	17.59	7.27	1680.22	27.22	18.34	0.360
55	1697.99	17.59	7.78	1680.95	27.19	17.75	0.383
60	1698.39	17.41	8.03	1681.73	27.18	16.64	0.407
15/85							
40	1696.48	17.94	8.41	1679.59	25.4	14.52	0.451
45	1696.96	18.07	8.90	1680.31	25.35	13.70	0.480
50	1697.39	18.11	9.32	1680.97	25.28	13.04	0.504
55	1697.82	18.12	9.71	1681.65	25.28	12.46	0.525
60	1698.22	18.11	10.05	1682.34	25.27	11.92	0.545
65	1698.64	18.09	10.40	1683.04	25.31	11.40	0.564
20/80							
40	1696.57	18.04	11.18	1680.22	24.45	13.79	0.535
45	1697.09	18.14	11.82	1681.00	24.35	12.87	0.566
50	1697.5	18.22	12.49	1681.68	24.21	11.99	0.597
55	1697.97	18.26	13.08	1682.48	24.14	11.14	0.625
60	1698.38	18.28	13.48	1683.18	24.18	10.59	0.644
65	1698.72	18.27	13.80	1683.81	24.22	10.13	0.659
25/75							
40	1696.86	18.11	12.50	1681.21	23.73	10.32	0.632
45	1697.23	18.18	12.61	1681.72	23.79	9.86	0.645
50	1697.71	18.27	12.92	1682.49	23.86	9.22	0.665
55	1698.06	18.35	13.40	1683.11	23.85	8.70	0.686
60	1698.53	18.38	13.90	1684.00	24.11	8.41	0.701
65	1698.96	18.46	14.15	1684.86	24.33	8.05	0.714
30/70							
40	1696.84	18.34	14.13	1681.40	22.88	9.05	0.689
45	1697.35	18.75	13.52	1682.04	23.12	7.96	0.707
50	1697.75	18.84	13.94	1682.81	23.27	7.48	0.726
55	1698.20	18.71	13.79	1683.67	23.83	7.49	0.723
60	1698.70	18.74	13.99	1684.84	24.36	7.23	0.733
65	1699.08	18.71	13.96	1685.78	24.89	7.25	0.732
40/60							
40	1696.92	18.43	15.46	1682.39	22.68	7.13	0.755
45	1697.50	18.6	16.35	1683.76	23.44	7.09	0.766
50	1697.89	18.55	15.88	1684.45	23.69	6.62	0.773
55	1698.39	18.70	15.58	1685.83	24.52	6.75	0.766
60	1698.75	18.72	15.57	1686.73	24.87	6.66	0.768
65	1698.98	18.66	15.93	1687.38	24.96	6.69	0.772

[a] HB-hydrogen bonded. [b] $f_F^{C=O}$ represents the fraction of free carbonyl groups in the mixture defined in eq 14. [c] This fraction represents the molar ratio of NEP molecules versus ethanol molecules. The concentration of NEP molecules in the mixture is constant and equal to 0.04 mol L^{-1}.

Table 2. Curve-Fitting Results of PVP/Ethanol Mixtures Diluted in CCl_4

T (°C)	free center (cm^{-1})	C=O width (cm^{-1})	band area	HB center (cm^{-1})	C=O width (cm^{-1})	band area	$f_F^{C=O}$
5/95							
40	1683.63	23.03	5.97	1666.49	27.59	10.90	0.412
45	1684.08	23.13	5.98	1666.92	28.00	10.76	0.416
50	1684.31	23.16	6.21	1667.10	27.73	10.47	0.431
55	1684.55	23.19	6.34	1667.28	27.60	10.22	0.443
60	1684.97	23.16	6.47	1667.66	27.54	9.90	0.456
65	1685.30	23.21	6.61	1667.96	27.49	9.56	0.469
8/92							
40	1683.94	22.90	6.30	1666.80	27.96	9.87	0.449
45	1684.18	22.91	6.42	1666.98	27.7	9.53	0.463
50	1684.61	22.87	6.52	1667.38	27.63	9.24	0.474
55	1684.92	22.86	6.66	1667.66	27.62	9.06	0.485
60	1685.30	22.85	6.74	1668.03	27.64	8.76	0.496
65	1685.71	22.81	6.80	1668.47	27.67	8.47	0.507
10/90							
40	1684.31	22.51	7.19	1667.30	27.34	9.77	0.485
45	1684.64	22.57	7.26	1667.59	27.24	9.32	0.499
50	1685.12	22.52	7.38	1668.08	27.16	8.93	0.514
55	1685.51	22.49	7.61	1668.50	27.12	8.70	0.528
60	1685.90	22.43	7.69	1668.94	27.16	8.44	0.539
65	1686.39	22.37	7.84	1669.53	27.19	8.17	0.551
13/87							
40	1684.56	22.51	7.45	1667.64	27.36	8.97	0.515
45	1684.98	22.49	7.69	1668.01	27.06	8.57	0.535
50	1685.53	22.43	7.78	1668.66	27.09	8.19	0.549
55	1685.84	22.42	7.85	1669.02	27.07	7.87	0.561
60	1686.33	22.32	8.00	1669.65	27.22	7.75	0.569
65	1686.82	22.25	8.09	1670.33	27.36	7.52	0.579
18/82							
40	1685.08	22.33	7.91	1668.38	27.46	7.97	0.560
45	1685.65	22.20	8.09	1669.09	27.26	7.62	0.576
50	1685.97	22.17	8.22	1669.48	27.25	7.48	0.584
55	1686.44	22.09	8.25	1670.18	27.36	7.26	0.593

[a] This fraction represents the molar ratio of PVP repeat units versus ethanol molecules. The concentration of PVP repeat units in the mixture is constant and equal to 0.04 mol L^{-1}.

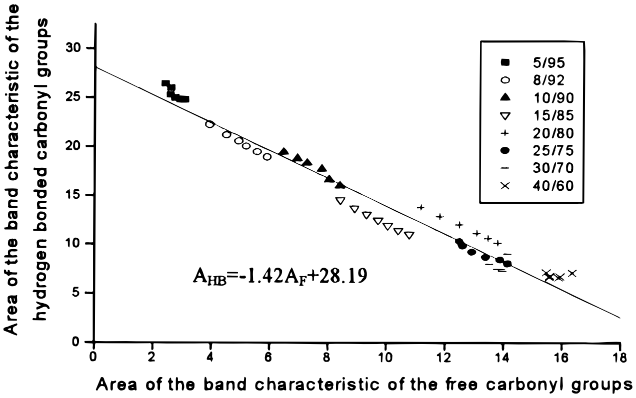

Figure 2. Plot of the area of the hydrogen-bonded carbonyl band versus the area of the free carbonyl band for NEP/ethanol mixtures at various temperatures and ethanol concentrations.

concentration of the hydrogen-bonded carbonyl groups decreases with increasing temperature. All data points are scattered around a line whose slope is the negative of the ratio of the absorptivity coefficients, $\alpha = a_{HB}/a_F$. These ratios along with one standard deviation are

$$\alpha_{NEP} = 1.40 \pm 0.04 \qquad \text{and} \qquad \alpha_{PVP} = 1.3 \pm 0.1$$

In Figure 3, we can notice consistent deviations of the data at a given ethanol concentration. The deviations could be due to a slight degradation of PVP with temperature which would affect the absorptivity coefficients of the carbonyl band.

The fraction of free carbonyl groups in any PVP/ethanol or NEP/ethanol mixture can be calculated using the equation

$$f_F^{C=O} = \frac{\phi_{A1}}{\phi_A} = \frac{A_F}{A_F + A_{HB}/\alpha} \tag{14}$$

Tables 1 and 2 show that for both PVP/ethanol mixtures and NEP/ethanol mixtures, the fraction of the free carbonyl groups increases when the temperature increases or when the ethanol mole fraction decreases. As

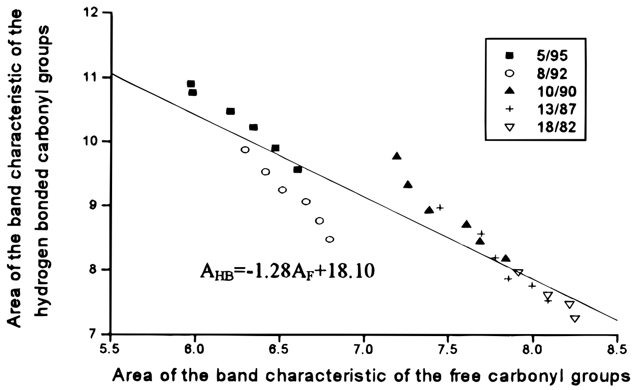

Figure 3. Plot of the area of the hydrogen-bonded carbonyl band versus the area of the free carbonyl band for PVP/ethanol mixtures at various temperatures and ethanol concentrations.

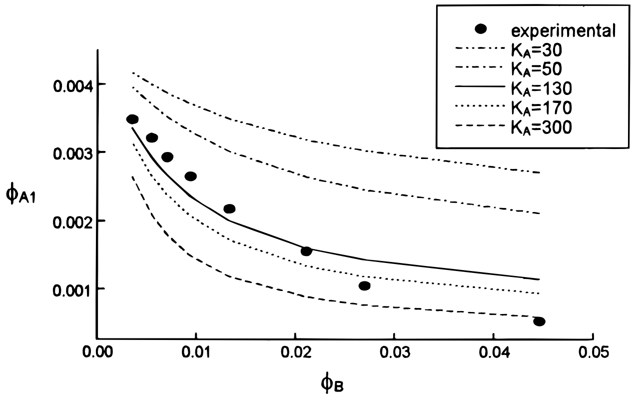

Figure 4. Comparison of the theoretical and the experimental values of the volume fraction of free carbonyl groups versus the volume fraction of ethanol groups in NEP/ethanol/CCl$_4$ mixtures at $T = 45$ °C. The theoretical values were calculated for $K_A = 30$, 50, 130, 170, and 300.

the ethanol concentration decreases, fewer hydrogen bonds can be formed. As the temperature increases, the hydrogen bonds become weaker and fewer in number. For a given temperature or ethanol concentration, the mole fraction of free carbonyl groups is always lower for the NEP/ethanol mixtures than for the PVP/ethanol mixtures. The formation of hydrogen bonds between ethanol and the small NEP molecules appears to be more favorable than between ethanol and the polymeric molecules, presumably due to the additional conformational restrictions imposed on the polymer.

Determination of the Interassociation Equilibrium Constants. The interassociation equilibrium constant, K_A, can be determined by choosing a value for K_A and calculating the theoretical values of ϕ_{B1} and ϕ_{A1} by simultaneously solving eqs 5 and 6 for given values of ϕ_A and ϕ_B. The value of K_A is then systematically varied and the best fit of the experimental data was determined. For these calculations, the values of K_2 and K_B were previously determined.[31] Alternatively, one could determine the best fit of the experimental data while systematically varying the values of the three equilibrium constants. However, because many different solutions can be found to fit the experimental data,[11] the two self-association constants need to be determined independently.

The graphs presented in Figures 4 and 5 show the experimental and the theoretical values of the volume fraction of free carbonyl groups, ϕ_{A1}, as a function of the volume fraction of ethanol in NEP/ethanol/CCl$_4$ and PVP/ethanol/CCl$_4$ blends for different values of K_A at $T = 45$ °C. At this temperature, and for volume fraction of ethanol ranging from 0 to 0.05, the best curve-fit of the experimental data was found for $K_A = 130 \pm 5$ in terms of volume fractions for NEP/ethanol/CCl$_4$ mixtures and for $K_A = 70 \pm 5$ in terms of volume fractions for PVP/ethanol/CCl$_4$ mixtures. The same curve-fitting procedure was followed in the analysis of the data given in Tables 1 and 2 for temperatures ranging from 40 to 65 °C. Table 3 summarizes the values of K_A found at each temperature.

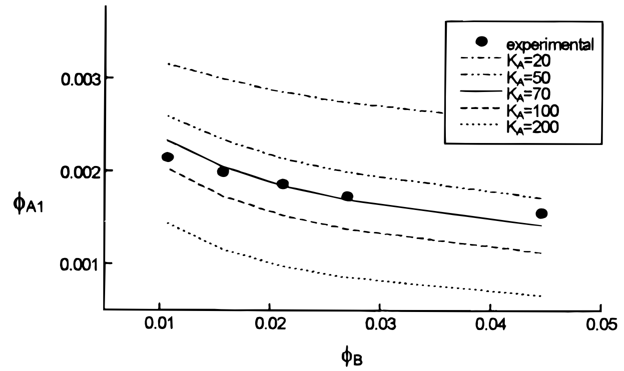

Figure 5. Comparison of the theoretical and the experimental values of the volume fraction of free carbonyl groups versus the volume fraction of ethanol groups in PVP/ethanol/CCl$_4$ mixtures at $T = 45$ °C. The theoretical values were calculated for $K_A = 20$, 50, 70, 100, and 200.

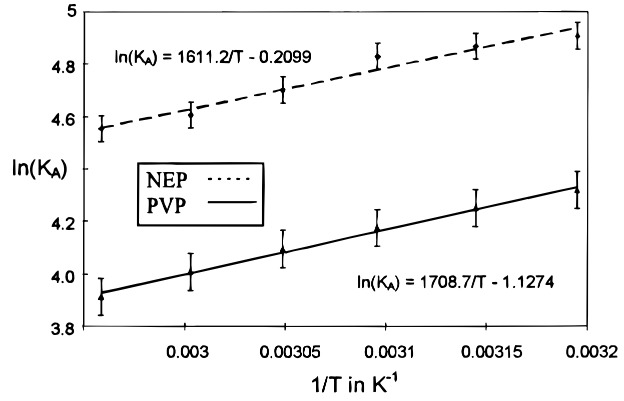

Figure 6. van't Hoff plot for the determination of Δh_A for NEP/ethanol/CCl$_4$ and PVP/ethanol/CCl$_4$ mixtures.

Table 3. Values of K_A in Terms of Volume Fraction (Dimensionless Number) Determined for NEP/Ethanol/CCl$_4$ and PVP/Ethanol/CCl$_4$ Mixtures

T (°C)	40	45	50	55	60	65
NEP	135	130	125	110	100	95
PVP	75	70	65	60	55	50

Assuming that the enthalpy of hydrogen bond formation between A and B units is independent of temperature, the enthalpy, Δh_A, can be determined by plotting ln K_A versus $1/T$. The slope of the curve-fitted line is equal to $-\Delta h_A/R$. These plots are presented for both NEP–ethanol and PVP–ethanol interactions in Figure 6. The enthalpy of hydrogen bond formation between NEP and ethanol was found to be equal to -3.2 kcal mol^{-1} and to -3.4 kcal mol^{-1} for PVP and ethanol. This compares with literature vales of 1–10 kcal mol^{-1} for hydrogen bond formation.[2] At $T = 25$ °C, the values of the interassociation equilibrium constants, K_A, in terms of volume fraction are 180 for NEP mixtures and 100 for PVP mixtures.

In Figures 4 and 5, we can see that the experimental measurements of ϕ_{A1} deviate from the theoretical curves

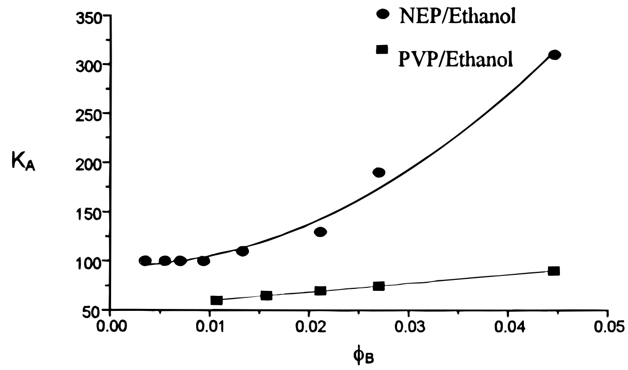

Figure 7. Plot of K_A versus ϕ_B for NEP/ethanol and PVP/ethanol mixtures diluted in CCl_4 at $T = 45$ °C

calculated for a given interassociation equilibrium constant. As the parameters K_2, K_B, K_A, and α were varied within the margins of errors, the experimental values of ϕ_{A1} still deviated from the predicted theoretical curves with the same trend. This proves that the deviations cannot be explained by errors in the determination of these parameters. We believe that these deviations come from a dilution effect that the model does not take into consideration. Indeed, NEP or PVP and ethanol are diluted in CCl_4 at volume fractions lower than 0.05. In such dilute solutions, CCl_4, in this case, can act as a screen between the carbonyl and hydroxyl groups and prevent the formation of hydrogen bonds. The value of K_A would then change with the volume fraction of ethanol in the mixture, ϕ_B. Furthermore, as the ethanol concentration decreases in the mixtures, the average number of self-associated ethanol units or the length of the chains, h, decreases. When h decreases in the expression for K_A given in eq 2, the value of the ratio $hr/(h + r)$ decreases and thus the value of K_A should decrease.

The values of K_A giving the same theoretical solution (obtained by the simultaneous solution of eqs 5 and 6) and experimental values for ϕ_{A1} at one given ϕ_B were determined. Figure 7 presents the variation of K_A with ϕ_B for both PVP/ethanol and NEP/ethanol mixtures. K_A increases as the volume fraction of B units increases. The ethanol concentration appears to have more of an effect on K_A for NEP/ethanol mixtures than for PVP/ethanol mixtures. Indeed, one can envision PVP forming hydrogen bonds primarily with short self-associated chains of ethanol because of steric effects. Conformational effects in PVP may also restrict access of larger self-associated ethanol chains. On the other hand, the smaller NEP molecules can form hydrogen bonds with larger self-associated chains of ethanol. Thus, the value of h that appears in the expression of K_A given in eq 2 has less influence on the interassociation of PVP and ethanol than on the interassociation of NEP and ethanol.

Table 4. Segment Information

	ethanol	NEP	PVP
molar vol (mL mol^{-1})	58.7	114.1	92.62
mol wt (g mol^{-1})	46.07	113.16	111.14
solubility parameter (cal/ml)$^{0.5}$	12.7	10.5	12.5
deg of polymerization	1	1	12

Table 5. Association Information Used for Free Energy Calculations

	NEP/ethanol		PVP/ethanol	
	K^a at 25 °C	Δh (kcal mol^{-1})	K^a at 25 °C	Δh (kcal mol^{-1})
B self-association (dimers)	$K_2 = 18.4$	−4.61	$K_2 = 18.4$	−4.61
B self-association (multimers)	$K_B = 60.0$	−4.15	$K_B = 60.0$	−4.15
A−B inter-association	$K_A = 180$	−3.2	$K_A = 100$	−3.4

[a] These values were determined for volume fractions of ethanol ranging from 0 to 0.05.

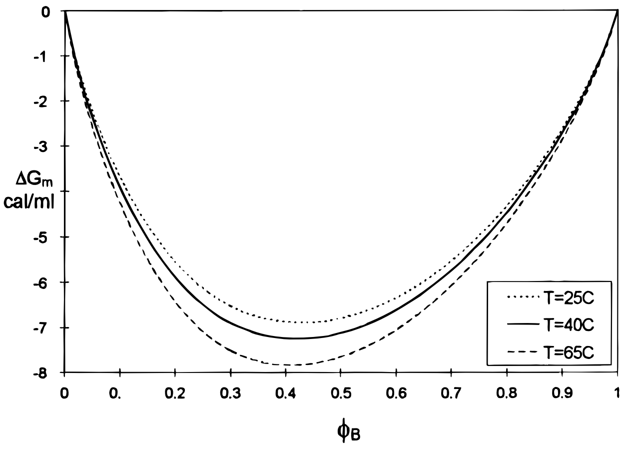

Figure 8. Free energy of mixing curves calculated at $T = 25$, 40, and 65 °C for a PVP/ethanol mixture.

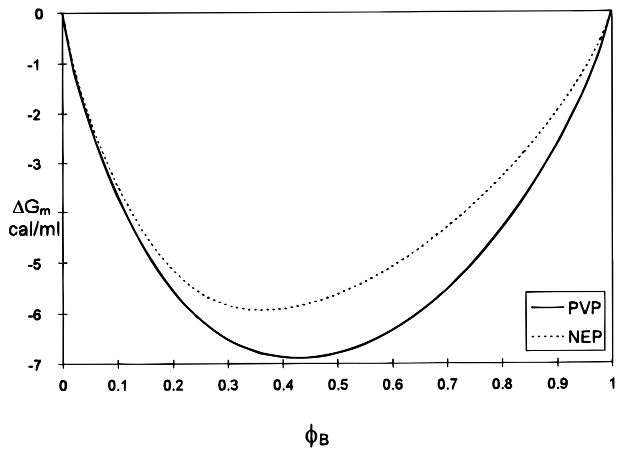

Figure 9. Free energy of mixing curves calculated at $T = 25$ °C for PVP/ethanol and NEP/ethanol mixtures.

Determination of the Energy of Mixing Curves. Using the parameters determined previously, the value of the Gibbs free energy of mixing was calculated using the MG&PC software developed by Coleman et al.. All the parameters used in the calculations are summarized in Tables 4 and 5. Average values of the interassociation equilibrium constants, K_A, determined for molar volumes of ethanol ranging from 0 to 0.05 were employed. Ideally, we wanted to obtained results for ethanol concentrations higher than $\phi_B = 0.05$, but we were limited by the saturation of the FTIR spectra. Figure 8 presents the calculated free energy of mixing curves at different temperatures for a PVP/ethanol mixture. While these calculations are based on average values for K_A determined in dilute mixtures of PVP or NEP/ethanol in CCl_4, they do provide some qualitative insight into the mixing functions for PVP and NEP in ethanol. Figure 9 shows that the Gibbs free energy of mixing PVP with ethanol is smaller than the Gibbs free energy of mixing NEP with ethanol. Indeed, the Flory−Huggins parameter for NEP/ethanol mixtures calcu-

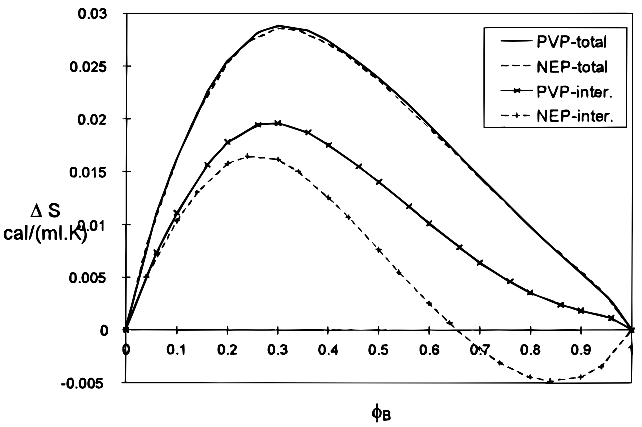

Figure 10. Total entropy of mixing and entropy of mixing due to interactions calculated for PVP/ethanol and NEP/ethanol mixtures.

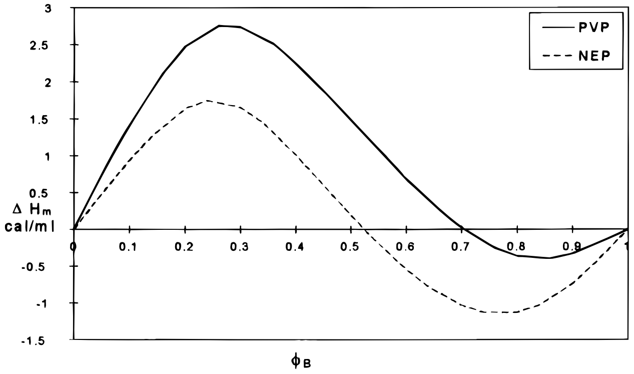

Figure 11. Enthalpy of mixing curves calculated for PVP/ethanol and NEP/ethanol mixtures.

lated using the group contribution method is larger than the one for PVP/ethanol mixtures. The term describing only the physical interactions, $\Delta G_m - \Delta G_H$, is thus larger for NEP mixtures than for PVP mixtures.

The enthalpy and the entropy of mixing can then be calculated using the equation

$$(\Delta G_m)_P = (\Delta H_m)_P - T(\Delta S_m)_P \tag{15}$$

Equation 15 is valid in a range of temperatures where ΔH_m and ΔS_m can be assumed to be independent of temperature. ΔH_m and ΔS_m are determined at a given mixture composition by plotting the values of ΔG_m versus temperature. Figure 10 shows that the total entropy of mixing NEP with ethanol or PVP with ethanol is quite similar. On the other hand, the entropy of mixing due to interactions, i.e. the total minus the ideal entropy of mixing, is larger for PVP/ethanol mixtures than for NEP/ethanol mixtures due to the fact that, at the same ethanol concentration, the fraction of hydrogen-bonded carbonyl groups is lower in PVP solutions. This suggests that the similarity of the entropy of mixing is fortuitous and comes from different types and numbers of interactions in the two mixtures. Figure 11 shows that at low ethanol concentrations, the mixing of NEP with ethanol or PVP with ethanol is endothermic and becomes exothermic as the ethanol concentration increases. At low ethanol concentrations when the fraction of hydrogen-bonded carbonyl groups is low, physical forces which are endothermic in nature are predominant in the mixture. At higher ethanol concentrations, more hydrogen bonds can be formed and exothermic specific interactions become predominant in the mixture. Figure 11 also shows that the enthalpy of mixing PVP with ethanol is always more positive than the enthalpy of mixing NEP with ethanol. At the same ethanol concentration, the fraction of hydrogen-bonded NEP units is higher than the fraction of PVP repeat units. Tables 1 and 2 show that at $T = 45$ °C, the fraction of free carbonyl groups, $f_F^{c=o} = 0.115$ for NEP/ethanol = 5/95, whereas for PVP/ethanol, $f_F^{c=o} = 0.416$. Since the formation of hydrogen bonds is an exothermic reaction, the enthalpy of mixing NEP with ethanol is expected to be more negative than the enthalpy of mixing PVP with ethanol.

Conclusion

Using the equilibrium constants for the formation of hydrogen bonds determined by infrared measurements, the Gibbs free energy of mixing PVP with ethanol and NEP with ethanol was calculated by employing a model for polymer systems with specific interactions developed by Coleman, Graf, and Painter. The free energy of mixing was found to be always negative and the NEP/ethanol and PVP/ethanol mixtures were shown to be miscible at any composition. Long PVP molecules appeared to form hydrogen bonds primarily with short self-associated chains of ethanol presumably because of steric and conformational effects. Smaller NEP molecules appeared to form hydrogen bonds with larger self-associated chains of ethanol. The total entropy of mixing ethanol with NEP was found to be very similar to the entropy of mixing ethanol with PVP. However, the entropy of mixing due to interactions was higher for PVP and ethanol than for NEP and ethanol. The mixing of ethanol with NEP or PVP was found to be endothermic at low ethanol concentration and exothermic at higher ethanol concentration. Also, the enthalpy of mixing NEP with ethanol was found to be more negative than the enthalpy of mixing PVP with ethanol at equivalent composition. Because of steric restrictions, more hydrogen bonds were formed in a NEP mixture than in a PVP mixtures at equivalent compositions. Since the enthalpy of hydrogen bond formation is negative, the enthalpy of mixing NEP with ethanol is expected to be more negative than the enthalpy of mixing PVP in terms of repeat units with ethanol.

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