

Temperature Dependence and Energetics of the Equilibrium Sorption of Water Vapor in Glassy Polyacrylonitrile

G. RANADE,* V. STANNETT, W. J. KOROS, *Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina*

Synopsis

Equilibrium sorption isotherms for water vapor in commercial polyacrylonitrile film are presented. The data are discussed in terms of the dual-mode sorption model at low vapor activities with cluster formation occurring at higher activities. The film samples were treated by a two-stage extraction process to remove a tenaciously held solvent present from the manufacturing process. Extraction of the residual had a minor effect on the equilibrium sorption of water in the film. The temperature dependence of the various sorption parameters is presented and discussed in detail.

INTRODUCTION

In a previous article, equilibrium sorption and transport data for water vapor in glassy polyacrylonitrile (PAN) films containing a small amount of residual solvent were presented over a limited range of activities and temperatures.¹ At low activities, the sorption data could be described by the dual-mode sorption model, while clustering of penetrant was evident at higher activities. The present article describes the effects on sorption results caused by removal of the trace residual solvent and expands the range of temperature studied beyond that of the previous investigation. Also, a more detailed analysis of the sorption process is presented, including the temperature dependencies of the various dual-mode sorption parameters, and an interpretation of various sorption enthalpy parameters derived from van't Hoff and isosteric analyses.

EXPERIMENTAL

A sample of biaxially oriented polyacrylonitrile film, approximately 0.5 mil thick, similar to that used for previous gas and water vapor studies, was obtained from the Sohio Co., Cleveland, OH, for the present study. Previously, the films were found to contain about 0.26% (by weight) of tenaciously held solvent even after prolonged boiling in water. It was found that this residual could be removed effectively by soaking the films overnight in benzene followed by boiling them in water for 144 hr the films used in the present study were treated in this way.

The equilibrium sorption measurements were made with a quartz helix McBain spring balance in a water jacketed chamber as described previously.¹

* Present address: Hooker Chemical Research Center, Niagara Falls, NY.

RESULTS

Sorption isotherms for water vapor in the PAN films at 15, 30, and 45°C are presented in Figure 1. The curves are quite similar in character to those reported earlier for PAN containing the 0.26% residual solvent. Data were measured at 30°C in both cases and the previous results¹ are included in Figure 1 for comparison. There is good agreement between the two sets of values, indicating that the presence of the residual has little apparent effect on the sorption of water vapor.

Zimm-Lundberg clustering parameters calculated from the data in Figure 1 for the residual-free films are presented in Figure 2. In the residual-free films, clustering begins to occur at a lower activity than in the earlier case for the film containing the trace residual solvent.¹ For the present double-extracted film shown in Figure 2, clustering begins to occur at an activity of about 0.45 at 15 and 30°C and at an activity of 0.4 at 45°C. In the earlier case, clusters were not observed below activities of 0.55–0.60. At higher activities, the data in Figure 2 indicate a significantly greater tendency to cluster as the temperature is increased. In rubbery polymers and hydrophobic liquids, the clustering process is exothermic, since movement of the surrounding chain segments or molecules can be accomplished with relative ease. It is possible, however, that in glassy polymers the inherently exothermic nature of cluster formation is overwhelmed by the energy required to separate chains to accommodate the cluster. It is reasonable, therefore, that the net process of cluster formation in glassy polymers is athermic or possibly slightly endothermic, while it is exothermic in rubbers. Barrie and co-workers² have noted somewhat similar effects for water clustering in their study of an homologous series of rubbery and glassy methacrylate polymers.

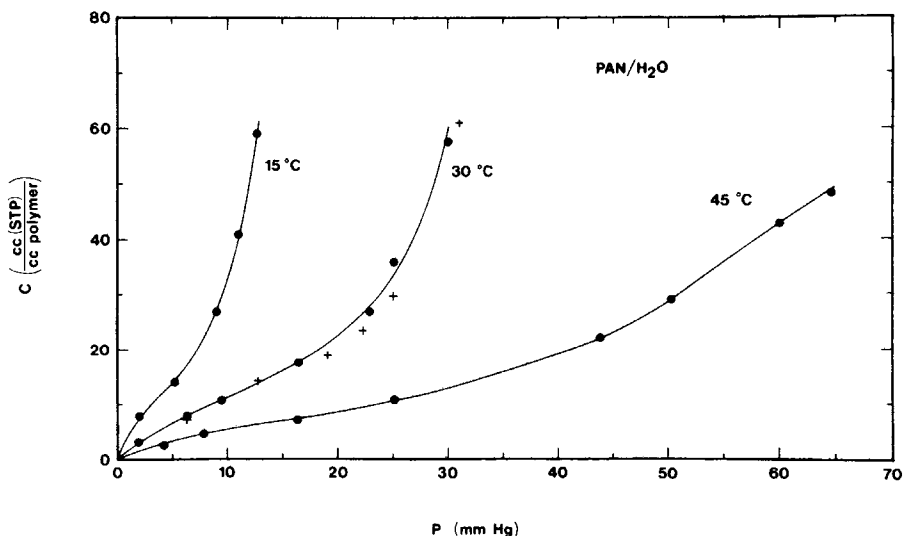


Fig. 1. Sorption isotherms for water in double-extracted PAN films at 15, 30, and 45°C. The + points correspond to earlier sorption measurements made for water vapor at 30°C in a PAN sample that contained 0.26% (by weight) of a tenaciously held solvent present from the manufacturing process. The double-extraction procedure removed this solvent.

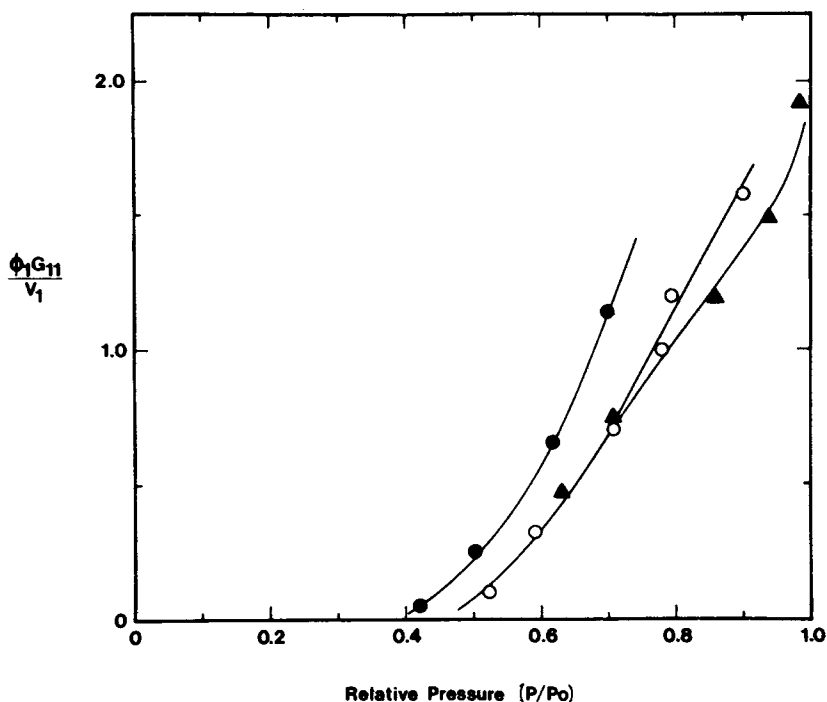


Fig. 2. Cluster size plotted vs. relative pressure for water in double-extracted PAN. (▲) 15°C; (○) 30°C; (●) 45°C.

Dual-Mode Sorption at Low Activities

At low vapor activities, the sorption isotherm shapes, concave to the pressure axis, are consistent with the dual-mode sorption model. The model is represented by the following equation³:

$$C = k_D p + C'_H b p / (1 + b p) \quad (1)$$

where C is the equilibrium concentration of water in the polymer at a pressure p , k_D is the Henry's law solubility coefficient cm^3 (STP)/(cm^3 polymer Torr), b is the Langmuir affinity constant (Torr^{-1}), and C'_H is the Langmuir sorption capacity cm^3 (STP)/ cm^3 polymer.

The dual-mode sorption parameters k_D , b , and C'_H were estimated by performing nonlinear regression analyses on the low activity sorption data in Figure 1. The temperature variations of the individual sorption parameters can be represented by van't Hoff relationships such as those given in eqs. (2) and (3):

$$k_D = k_{D_0} \exp(-\Delta H_D / RT) \quad (2)$$

where ΔH_D is the difference in enthalpy between the penetrant in the Henry's law dissolved state and in the vapor. Similarly,

$$b = b_0 \exp(-\Delta H_b / RT) \quad (3)$$

where ΔH_b is the difference between the enthalpy of the penetrant in the Langmuir-sorbed state compared to that in the vapor phase. The composite parameter $k_D + C'_H b$ is sometimes called the apparent Henry's law constant k_D^* and does not have a simple meaning in dual-mode systems, but nevertheless it

is often represented in a van't Hoff form with an apparent sorption enthalpy ΔH_D^* .

Van't Hoff plots for k_D , b , and k_D^* are shown in Figure 3. The values of the apparent sorption enthalpies obtained from these plots are -10.3 kcal/mole for ΔH_D , -11.7 kcal/mole for ΔH_b , and -13.5 kcal/mole for ΔH_D^* . The more negative value of ΔH_b as compared to ΔH_D is consistent with the fact that more energy is required for a molecule to separate chains and enter the Henry's law mode rather than to sorb into preexisting microvoids.⁴ The temperature dependence of C'_H can also be described phenomenologically by van't Hoff-type expressions such as eqs. (2) and (3) with an apparent sorption enthalpy ΔH^* . The apparent value of ΔH^* at 30°C calculated from the slope of the tangent of such a plot at 30°C is -3.5 kcal/mole. Based on the following interpretation of

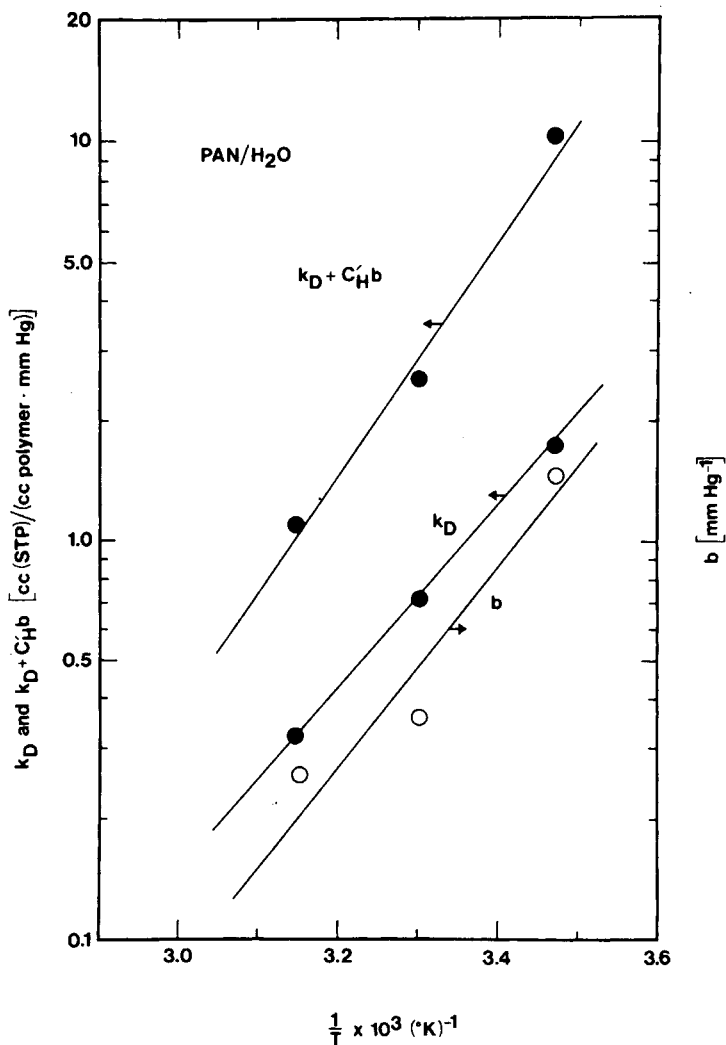


Fig. 3. Van't Hoff plots of the Langmuir affinity constant, b ($=$) (Torr) $^{-1}$, and the Henry's law constant, k_D ($=$) cm^3 (STP)/(cm^3 polymer Torr), k_D^* ($=$) cm^3 (STP)/(cm^3 polymer Torr) for water in double extracted PAN.

C'_H in terms of unrelaxed volume in the glass, it is likely that ΔH^* is not associated with a true heat effect which would be measured, for example, in isothermal calorimetry during the sorption process. The parameter ΔH^* , therefore, does not have a simple physical meaning analogous to that of ΔH_D and ΔH_b .⁵ The apparent Henry's law coefficient k'_D is considerably larger than k_D itself because of a significant contribution from Langmuir sorption. The difference between k'_D and k_D diminishes as the temperature increases and is expected to reach zero at T_g , where C'_H equals zero. This results in the more dramatic temperature dependence for k'_D compared with both k_D and b . The 3.2 kcal/mole difference between ΔH_D and $\Delta H'_D$ arises in part from the *apparent* enthalpy of sorption associated with the decrease in C'_H as the temperature increases; therefore, interpretation of the significance of the difference between the two parameters is confounded by the same factors mentioned for ΔH^* .

Figure 4 presents a plot of C'_H vs. T . The data approximate a straight line and extrapolate to about 85°C, which is near the glass-transition point of the polymer in the presence of water. The behavior shown in Figure 4 is consistent with the interpretation of C'_H offered by Koros and Paul,⁶ which predicts that C'_H should decrease roughly linearly with increasing temperature and disappear above T_g because of mobilization of microvoids existing as unrelaxed gaps between chain segments. The value of the Langmuir sorption capacity C'_H can be predicted using eq. (4) (ref. 6):

$$C'_H = \omega_a \frac{(dV/dT)_l - (dV/dT)_g}{V_g} (T_g - T) \frac{(22,400)\rho}{M_w} \quad (4)$$

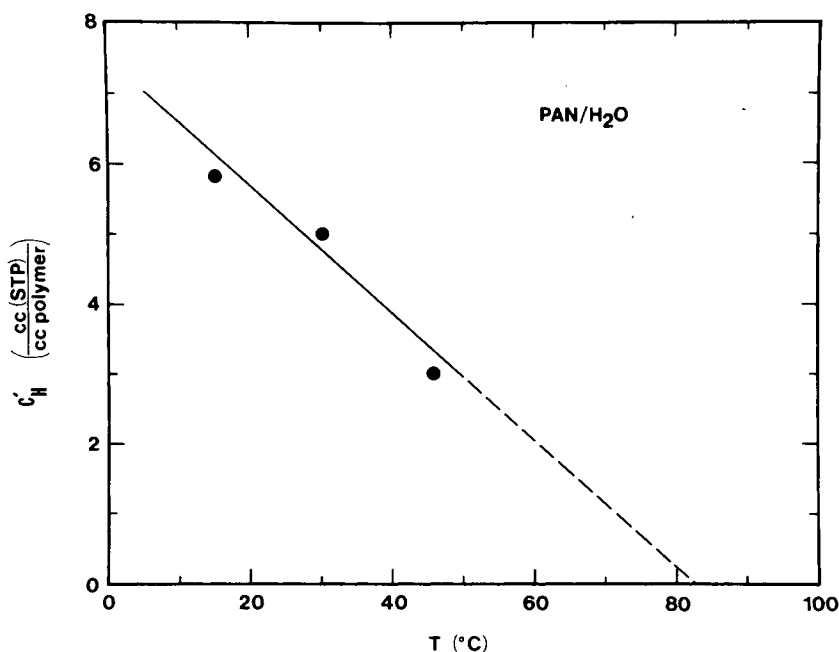


Fig. 4. Langmuir capacity constant C'_H plotted vs. temperature for water in double-extracted PAN. Note that C'_H appears to extrapolate to zero reasonably close to the polymer's T_g ($\approx 85^\circ\text{C}$) in the presence of water.

where $(dV/dT)_l$ and $(dV/dT)_g$ are the slopes of specific volume versus temperature lines in the rubbery and glassy states, respectively, for a purely amorphous polymer, ω_a is the amorphous fraction in the polymer, V_g is the actual specific volume of the glassy polymer, M_w is the molecular weight of the penetrant, and ρ is the mass density of the penetrant in the sorbed state.

Volume expansion data for an essentially amorphous PAN sample are reported by Beevers et al.⁷ The difference $[(dV/dT)_l - (dV/dT)_g]$ from their data is 1.02×10^{-4} cm³/g K. The density of the water in the sorbed state may be taken as 1 g/cm³ based on a suggested analogy between sorption in polymer microvoids and in zeolite microvoids.⁶ If the polymer amorphous fraction is assumed to be unity, the predicted values of C'_H are a factor of two larger than the experimental values in Figure 4. The discrepancy between the predicted and observed values of C'_H may be partly due to additional crystallinity which may have developed in the PAN film as a result of extraction of the film in water for a long period of time, i.e., ω_a is decreased. This possibility is supported by the physical appearance of the film which became slightly cloudy after extraction.

Cluster Formation at High Activities

An indication of clustering of penetrant molecules can also be obtained by observation of the variation of the Flory-Huggins χ value with penetrant activity for the material which is assumed to exist in the dissolved mode. The penetrant concentration in the dissolved mode can be obtained by subtracting the Langmuir component from the total isotherm. The values of χ that were determined for the 30°C isotherm were found to progressively decrease from 3.0 to 2.39 for activities of 0.45 to 0.99, respectively, again indicating the presence of clustering. This approach to the analysis of clustering has been discussed in detail by Williams et al.⁸

Isosteric Sorption Enthalpy

Finally, an isosteric enthalpy analysis of the data in Figure 1 was performed. The isosteric enthalpy ΔH_I is measured at a fixed concentration in the polymer and is given by

$$\frac{\Delta H_I}{R} = z \left[\frac{d \ln p}{d(1/T)} \right]_C \quad (5)$$

where z is the compressibility factor and R is the gas constant. Figure 5 shows the variation of ΔH_I with concentration at 30°C determined from Figure 1. The variation of ΔH_I with concentration can be predicted using the expression given in eq. (6) for systems that obey dual-mode sorption theory⁵

$$\Delta H_I = z \left(\frac{k_D \Delta H_D + C'_H b \Delta H_{HT} / (1 + bp) - C'_H b^2 \Delta H_b p / (1 + bp)^2}{k_D + C'_H b / (1 + bp) - C'_H b^2 p / (1 + bp)^2} \right) \quad (6)$$

where $\Delta H_{HT} = \Delta H_b + \Delta H^*$. The solid line in Figure 5 was calculated using eq. (6), and the agreement with experimental points is good for concentrations below 10 cm³ (STP)/(cm³ polymer). The deviations between the calculated line

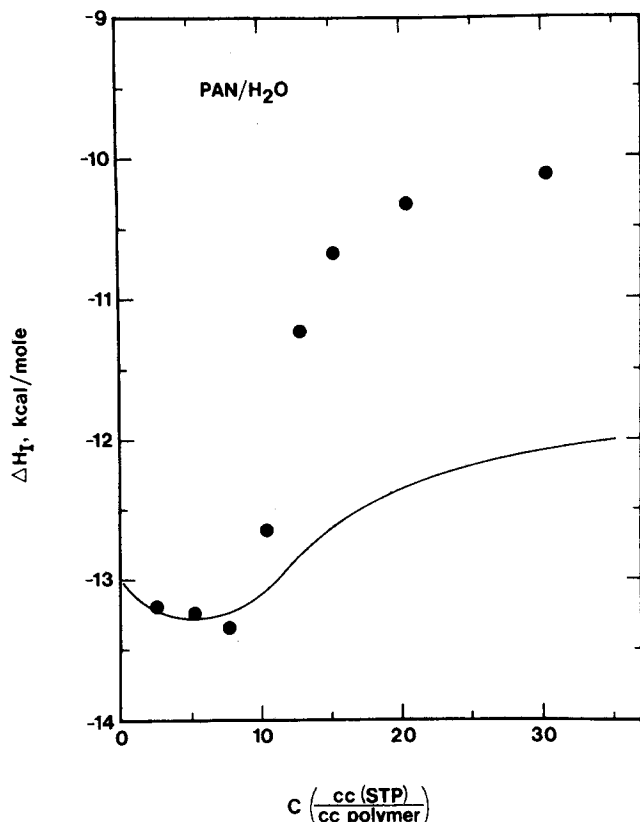


Fig. 5. Isosteric enthalpy of sorption for water in double-extracted PAN plotted vs. sorbed water concentration. Note that significant deviations from the theoretical line calculated from eq. (6) occur when cluster growth begins. The asymptotic limit of ΔH_I appears to approach the latent heat of condensation under the conditions studied.

and the data in Figure 5 at higher concentrations are presumably due to the onset of clustering, so that the simple dual-mode description of the sorption isotherm is no longer valid.

CONCLUSIONS

The detailed analysis of water vapor sorption offered here is consistent with the earlier preliminary analysis which suggested that simple dual-mode sorption occurs at low vapor activities and cluster formation occurs at high activities. The removal of a residual (0.26%) solvent had a rather small effect on sorption equilibria. The breakdown of the formal isosteric enthalpy analysis based on the simple dual-mode sorption isotherm occurs for concentrations near to that where clustering is suggested to occur by a Zimm-Lundberg-type analysis. It is anticipated that careful measurements may reveal that the features noted above for water sorption in PAN may, indeed, be rather generally present in many hydrophobic glassy polymers.

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