

# Dimethyl Acetamide Sorption Equilibria in a Urethane/Urea/Ether Block Copolymer

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## SYNOPSIS

A study of the interaction of solvent in a urethane/urea/ether copolymer belonging to the spandex family of materials is presented. Sorption and desorption isotherm data for *N,N*-dimethylacetamide (DMAc) in spandex solutions are used to determine thermodynamic parameters of solvent/polymer interaction. Isothermic enthalpies for sorption of DMAc tend to approach the heat of evaporation of DMAc at high sorbed concentrations. A qualitative mechanism for assemblage of hard-segment domains in the polymer during desorption is presented and interpreted in terms of the sorption isotherms and isothermic enthalpy data. The study provides useful insights into the influence of particulate additives, such as titanium dioxide (TiO<sub>2</sub>) in the solution.

## INTRODUCTION

Spandex polymers compose a class of thermoplastic elastomers with diverse applications including textile fibers and medical prosthesis.<sup>1-3</sup> It is important to characterize the polymer/solvent interactions to understand the coupling between the thermodynamics and kinetics of the solvent devolatilization process. *N,N*-dimethylacetamide (DMAc) and *N,N*-dimethylformamide (DMF) have been found to be good solvents for spandex materials and DMAc was chosen for this study.<sup>4</sup> This paper will analyze sorption behavior for DMAc in the spandex polymer as a function of vapor activity and temperature. A subsequent paper will report data for desorption kinetics under controlled isothermal conditions to provide diffusion coefficients as a function of polymer phase concentration and temperature.

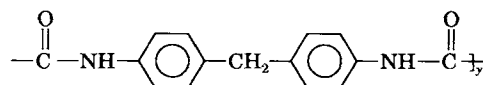
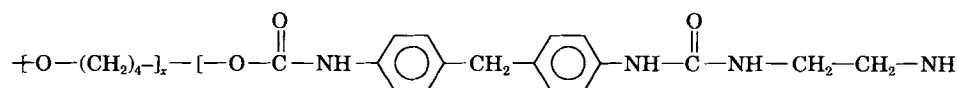
This study was also formulated to allow consideration of the effects of additives, specifically a whitening agent titanium dioxide (TiO<sub>2</sub>) on the equilibria between DMAc and the potentially two-

phase spandex polymer. The TiO<sub>2</sub> might be expected to act as a heterogeneous nucleating agent for the hard-segment domain assemblage process. The current study provides information pertinent to testing this expectation.

## EXPERIMENTAL

One type of spandex used in this study is transparent and referred to as "clear." The presence of  $\approx 2.0\%$  TiO<sub>2</sub> as a whitening agent in some samples transforms it to a white opaque material that will be designated as "white."

The spandex polymer is a segmented polyurethane consisting of a hard segment (a urea), melting above 200°C, and a soft segment (a polyether glycol), melting at approximately 50°C. Both segments are polymeric and connected by urethane linkages. The polymer forms a clear viscous solution in DMAc. The white solutions are identical to the clear except for the addition of small amounts of TiO<sub>2</sub> pigment. The general structure of the spandex polymer is shown below<sup>5</sup>:



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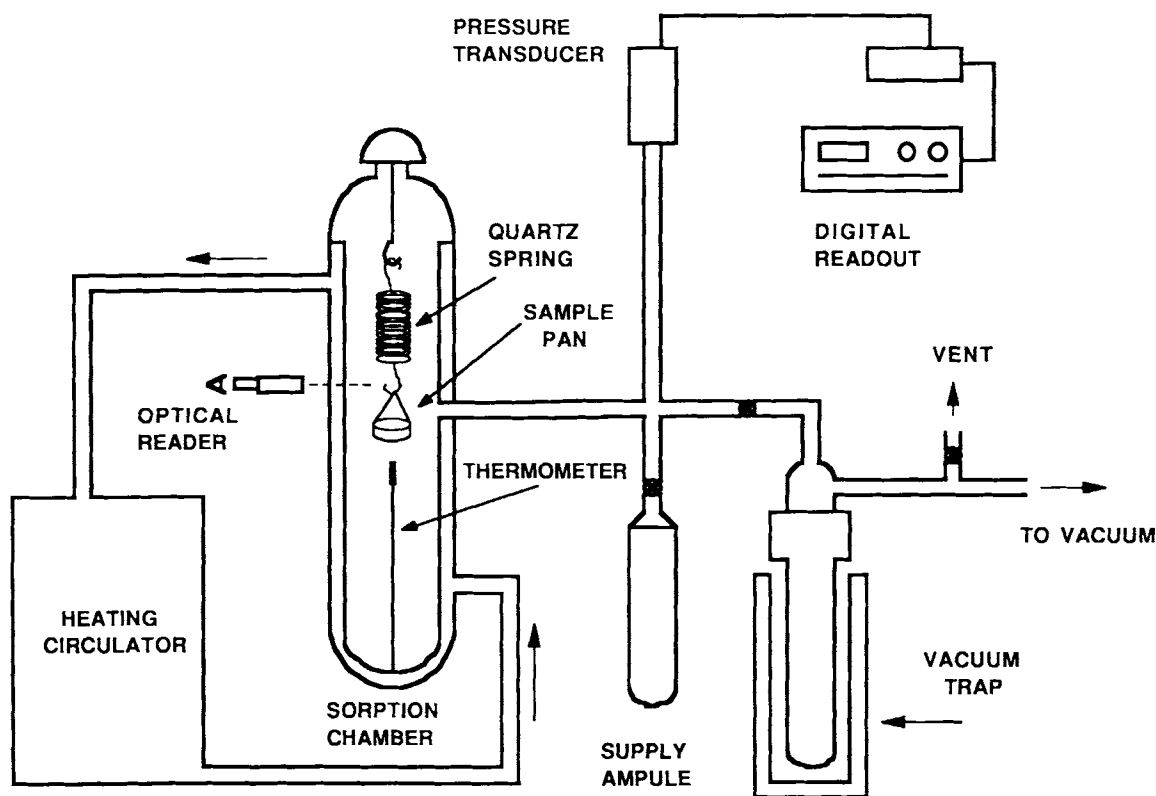
where  $x = 15-30$  and  $y = 1-5$ .

The equipment used for studying solvent sorption and desorption into and out of the polymer solution is based on a gravimetric measurement technique.<sup>6-12</sup> The polymer samples are placed in tared aluminum pans and are hung from the spring in the sorption chamber. Sensitive quartz springs are used in obtaining weight measurements by measuring the weight of the polymer sample directly as it sorbs or desorbs. Also, within the chamber, a quartz rod with calibrated reference nodes hangs next to the spring to allow simple readjustment of zero points for readings beyond the initial reference point of the optical reader. The optical reader used to measure the spring elongation consists of a filar eyepiece with a magnifying lens that was obtained from Sherwood Instruments, Dallas, TX. The eyepiece is capable of readings in the order of 0.025 mm and the springs have an accuracy of 0.01 mg/mm, thereby making the system sensitive to sorption levels of 0.0025 mg or 2.5  $\mu\text{g}$ .

A schematic of the sorption chamber with its supporting equipment is shown in Figure 1. The chamber is a double-walled vessel maintained at constant temperature by a Lauda circulator filled

with a water and ethylene glycol mixture in order to achieve high temperatures. The supply ampule and the rest of the system is kept isothermal by means of heating tapes and fiberglass insulating tapes. A high-temperature pressure transducer, MKS Baratron Type 510A, is used to monitor the system pressure. A liquid nitrogen cold trap is connected to a Duo Seal Edwards vacuum pump to condense the vapor as it leaves the system during desorption.

Experimental runs were performed at a constant temperature. The sample was placed in a tared aluminum sample pan and suspended from the spring into the chamber. The system was then evacuated slowly to prevent bubbling of the sample. The supply ampule was also exposed to vacuum to ensure that all air above the solvent had been removed. The DMAc in the ampule was prepurified by distillation to remove trace impurities. As the system pressure was lowered to the saturated vapor pressure of the DMAc solvent for that temperature, the supply ampule was opened to allow solvent vapor into the chamber and prevent drying of the sample. This procedure was repeated several times until no air



**Figure 1** Schematic of the sorption cell with supporting equipment used in sorption equilibria studies.

remained in the system. The initial position of the spring was recorded to determine the weight of the saturated sample.

The data for the isotherms were obtained by decreasing the vapor pressure in the chamber in steps of 5–10 mmHg and allowing the sample to reach equilibrium. As DMAc desorbs, the weight of the sample decreases, and it is measured by the change in length of the spring. Equilibrium for a specific vapor pressure is reached when the polymer no longer desorbs more penetrant and the spring remains at a fixed position. After reaching equilibrium at "total" vacuum ( $< 50 \mu\text{Hg}$ ), the sorption isotherm was obtained by increasing the pressure of vapor in the chamber with the aid of the supply ampule. Again, equilibrium measurements were recorded, this time from vacuum to the saturated vapor pressure of DMAc at the respective temperature being studied. After obtaining the weight and equilibrium readings, the system was evacuated again to completely dry the sample. When the sample was dry, the vacuum was released, and the sample was removed from the system and quickly weighed to obtain the mass of the dried polymer needed to calculate the uptake.

Buoyancy corrections were negligible, and there was negligible solvent adsorption by the spring or sample pan at pressures below saturation as determined by blank runs.

## BACKGROUND

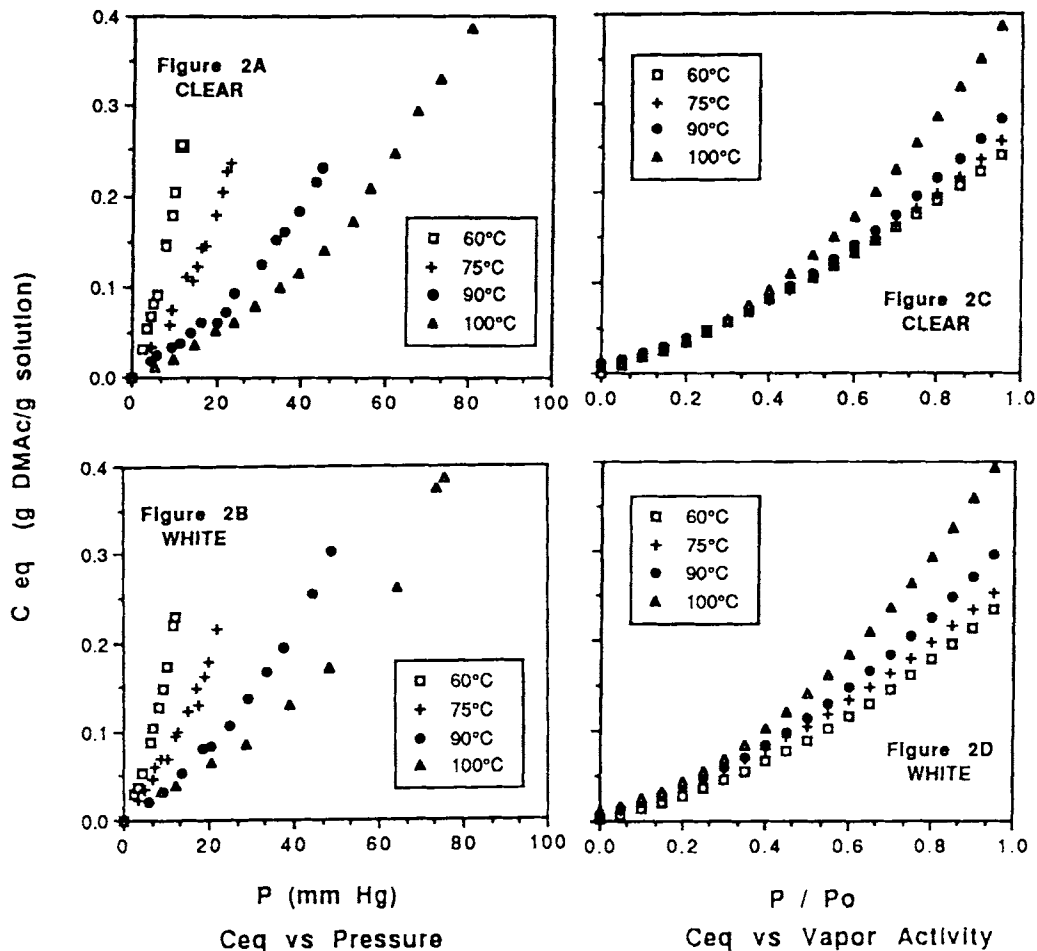
In general, polyurethane elastomers are block copolymers with relatively short polyurethane segments separating long, flexible polyether or polyester blocks. The ether or ester segments are usually soft and provide the material its elastic qualities, while the hard segments provide the necessary strength for a useful modulus by physical cross-links. In the present family of materials, the hard-segment domains are actually urethane-terminated ureas. In solutions, desorption is generally thought to occur from a more or less homogeneously unaggregated random mixture of both hard and soft segments at high solvent activity. Instrumental analyses including X-ray<sup>13,14</sup> and small-angle light scattering<sup>15</sup> indicate, however, that at some solvent activity a microphase-separated morphology exists composed of hard segment domains embedded in a soft elastomeric matrix. Based on differential scanning calorimetry (DSC) and thermomechanical analysis (TMA), Clough et al.<sup>16</sup> concluded that the ordering of molecules occurs to a higher degree in polyether-

based polyurethanes than in those where the flexible portions were polyester-based due to easier achievement of hydrogen bonding between urethane/urethane groups provided by the highly flexible polyether soft segments. It was also suggested from Clough et al.'s work<sup>17,18</sup> that the occurrence of microphase separation or domains appears to be enhanced by the existence of longer urethane blocks. The current spandex material, therefore, as a polyether-based, long-chained urethane polymer, is expected to have a large degree of local ordering in its matrix and a high degree of microphase separation.

## RESULTS AND DISCUSSION

Sorption equilibria of DMAc into the spandex polymer, both clear and white, are shown in Figure 2 (A) and (B). The figure shows plots of weight fraction of DMAc (grams DMAc/total grams) versus the partial pressure of DMAc in the cell for temperatures ranging from 60 to 100°C. The isotherms obtained are of type III in the Brunauer classification.<sup>18</sup> These isotherms are of a form typical of most polymer solutions, particularly of plastics and threads.<sup>19</sup> The graphs in Figure 2 (C) and (D) are equilibrium values for clear and white spandex plotted as a function of vapor activity for better comparison of the sorption levels at different temperatures. Equilibrium levels are higher for the same activities at higher temperatures. The curves on the activity plots represent an averaged value of the sorption level in the polymer for several runs under the same experimental conditions fitted to second-order polynomial equations.

The sorption data at constant temperatures as a function of spandex type are shown in Figure 3. The graphs are plots of equilibrium concentration versus vapor activity. It is interesting to note that the clear spandex sorbs a larger amount of solvent than does the white spandex at the lower temperature, that is, 60°C. At 75°C, there is no detectable difference in the amount of DMAc sorbed by the two samples, and as the temperature is increased to 100°C, the sorption level of the white spandex becomes slightly larger than that of the clear sample. To understand the effect of TiO<sub>2</sub> on the sorption levels of a sample, a hypothesis of the mechanism of aggregation in block or segmented copolymers is presented. A model for the structure formation in polyurethanes was described by Chang and Wilkes.<sup>20</sup> This work was carried out to determine the superstructure and domain morphology in segmented polyether urethanes that were capable of forming hydrogen bonds



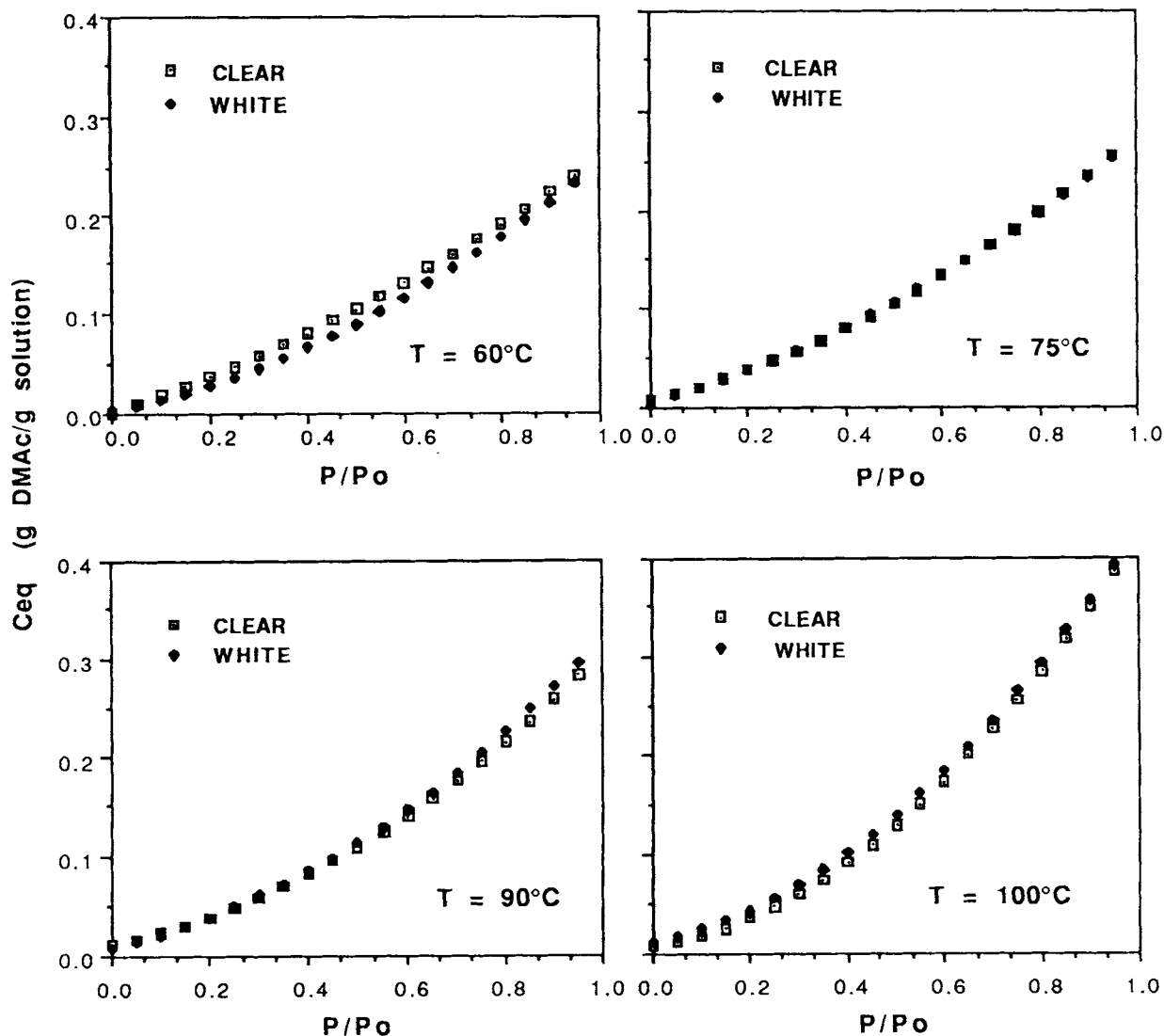
**Figure 2** Isotherms for clear and white spandex at temperatures ranging from 60 to 100°C. Isotherms are plotted as a function of pressure,  $P$ , in (A) and (B) and as a function of activity,  $P/P_0$ , in (C) and (D).

and whose hard segment domains initially had a low degree of order. The overall morphology is proposed to be formed by the initial aggregation of hard segments into domains and subsequent assemblage of the hard-segment domains into superstructures. The superstructure formation is achieved by the following steps:

- I. Nucleation takes place between two chains.
- II. The compatibility and hydrogen bonding between hard segments brings more hard segments together, stabilizing the nucleus and promoting local aggregation of hard segments.
- III. Further growth of the nucleus sets forth domain formation in the vicinity, leading to hard segment domains extending radially from the primary nucleus.

- IV. Segments on many molecules, which are not necessarily linked to the first nucleus, are brought into the superstructure and form more and larger hard segment domains, again, preferentially, radially oriented.

Since superstructure formation may have a significant influence on the sorption and desorption into and out of spandex solutions, it is important to understand the aggregation process and to determine how particulate additives might influence the process. In understanding the superstructure formation, it is helpful to differentiate between aggregation of hard segments to form domains as noted above and subsequent assemblage of these domains to form superstructures. The aggregation of hard segments to form domains is independent of the presence of additives in the solution, but small concentrations of



**Figure 3** Comparison of isotherms as shown in Figure 2 at specific temperatures for clear and white spandex. Trends in sorption ability of the two types of spandex with increasing temperature are examined.

heterogeneous nuclei within a polymer matrix may tend to promote the assemblage of the hard-segment domains.<sup>21</sup>

Additional details also are worthy of brief comments regarding the difference in clear and white samples shown earlier. At low temperatures and for the same external conditions, the white spandex, with the more effectively ordered superstructure, is able to sorb less solvent, as shown in Figure 3. As the temperature increases, however, domain disorder tends to increase,<sup>21</sup> apparently overcoming the ability of additives to promote superstructure formation. This effect might cause the slight increase in the sorption capacity of the white spandex at higher temperatures, as seen in Figure 3.

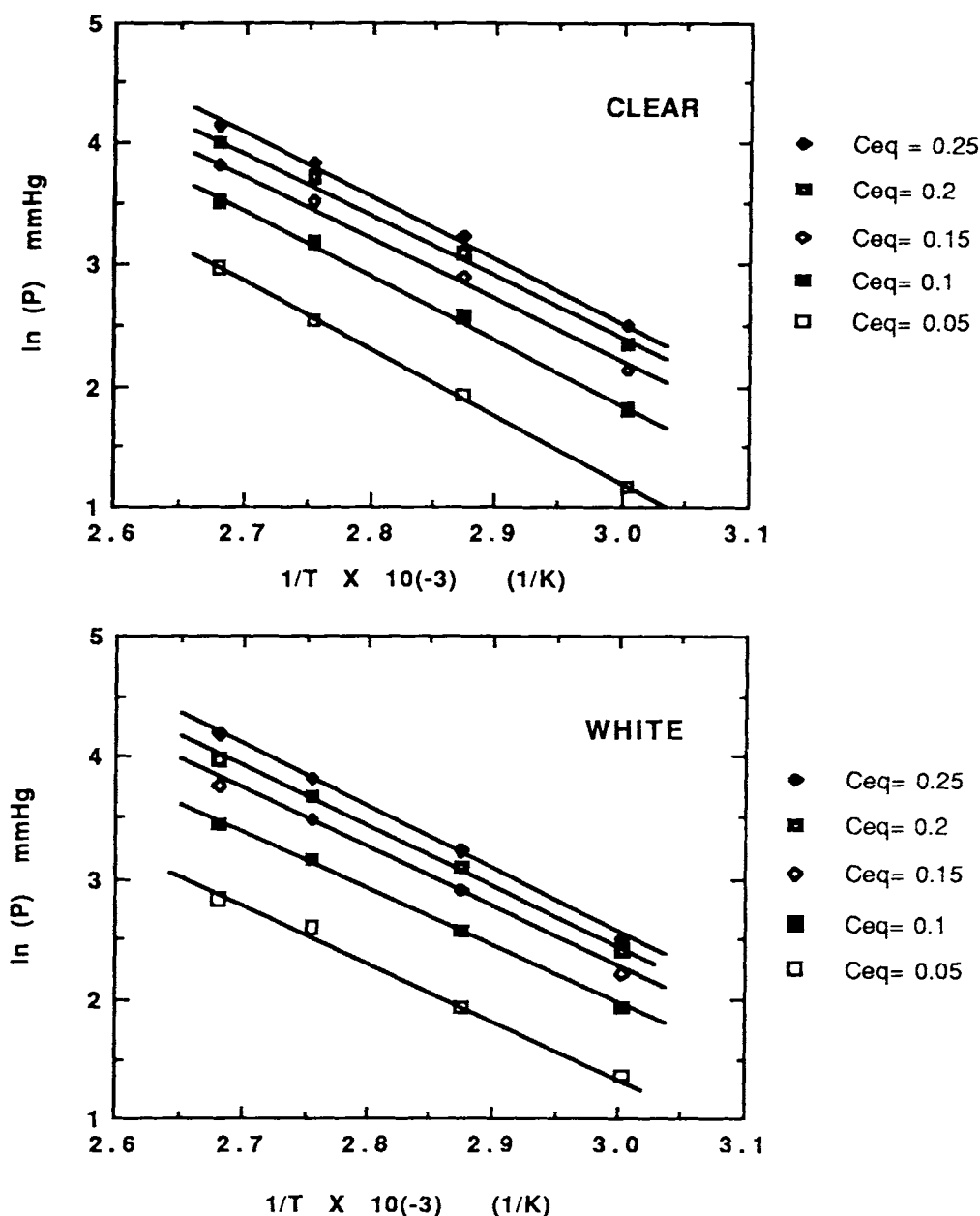
The effect of the  $\text{TiO}_2$  on the levels of sorption and the assemblage ability of the hard-segment domains can be examined further by considering the enthalpies of sorption for DMAC in both types of spandex solutions. The heat of sorption is defined as the amount of energy absorbed or released by a material when a gas or liquid is sorbed. The isosteric heat of sorption is a measure of the difference in enthalpy at a fixed sorbed concentration between a molecule in the sorbed state and in the gaseous state. The isosteric heat of sorption may be expressed by the relation<sup>22</sup>

$$\Delta H_{\text{ist}} = -RT^2 \left( \frac{\partial \ln p}{\partial T} \right)_c = R \left[ \frac{\partial \ln p}{\partial (1/T)} \right]_c \quad (1)$$

where  $p$  and  $T$  refer to the pressure and temperature of the system, respectively, and the subscript "c" designates conditions of constant concentration. To determine the enthalpies of sorption for DMAc in spandex, semilogarithmic plots of partial pressure versus inverse absolute temperature at constant sorption concentration were obtained from the equilibrium data presented earlier. The curves obtained, shown in Figure 4, are linearly decreasing with  $1/T$  for both clear and white types of spandex,

and since the temperature dependence on solubility obeys eq. (1), the heat of solution can be calculated.

The sorption process may be pictured as taking place in two stages: The first involves making a hole of molecular size in the polymer, which is an endothermic process. The second stage is transferring the molecule from the gas phase into the hole and allowing interactions between the molecule and the surrounding matrix, which is an exothermic process. The energy associated with the first process is de-

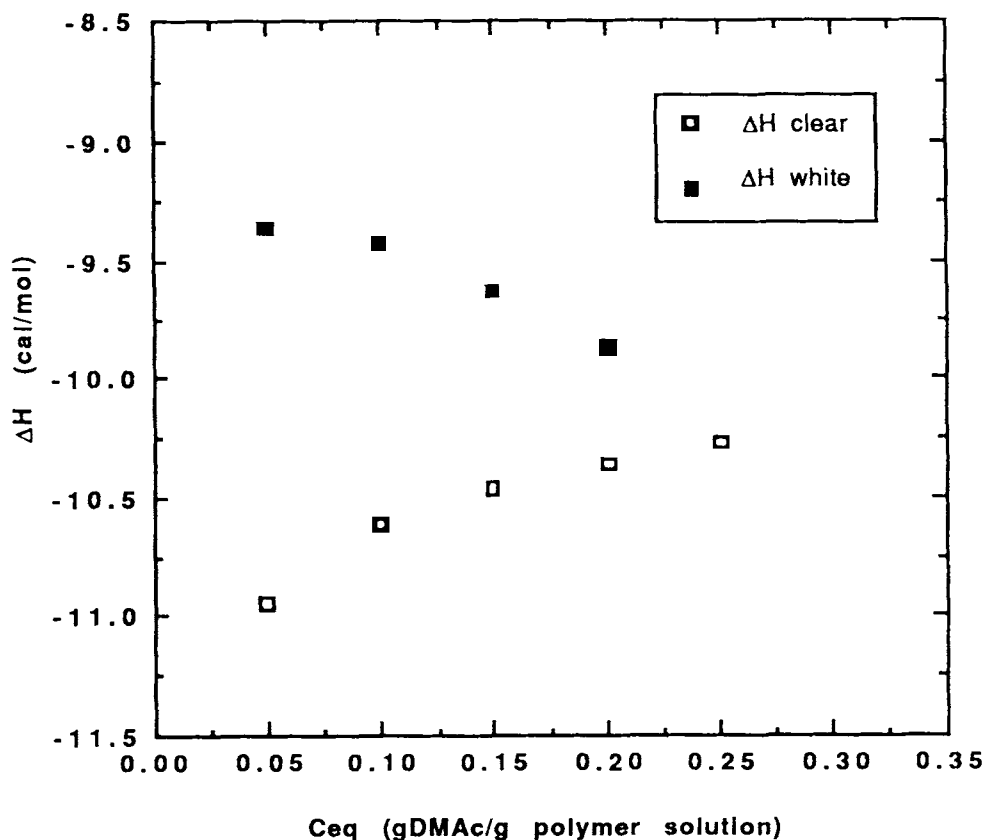


**Figure 4** Logarithm of pressure versus inverse temperature at constant concentrations of clear and white spandex as obtained from the equilibrium data. From these graphs, isosteric heats of sorption are calculated.  $C_{eq}$  in units of g DMAc/g solution.

pendent on the molecular volume of the gas and the cohesive energy density of the polymer. The energy evolved in the second stage is governed by the strength of the van der Waals, dipolar, or hydrogen bonds formed between the sorbed gas molecules and the surrounding polymer. The heat of sorption is the resultant energy from a combination of these two processes and is calculated from the slopes of the isosteres.

The values of  $\Delta H_{\text{ist}}$  thus obtained are plotted as a function of concentration in Figure 5. In comparing the heats of sorption of clear versus white type spandex, we note that the heat of sorption of the white spandex decreases with increasing solvent concentration and the heat of sorption of the clear spandex increases with increasing concentration. It is of importance that in spite of the fact that the lines have opposite slopes they asymptotically approach a value of  $\Delta H_{\text{ist}}$  approximately equal to 10.25 kcal/gmol as a function of solvent concentration. This is consistent with the fact that the heat of vaporization of DMAc is 10.36 kcal/gmol at 25°C.<sup>23</sup> The opposite signs of the slopes for the two samples

as they approach this value is believed to reflect the differences in the assemblage ability of the white spandex versus that of the clear sample. As implied by the superstructure formation mechanism, the assembled hard-segment domains in the white spandex exclude DMAc more effectively at high concentrations. Thus, the equilibrium sorption concentration at a given external vapor activity is usually higher for the clear than it is for the white. At equivalent concentrations, the heat of sorption is less negative for the white sample since the better aggregated hard-segment domains provide less accessible interaction points to DMAc as opposed to the looser superstructure of the clear material. Presumably, in the clear sample, fewer of the urea groups composing such regions are tied up with hydrogen-bonding interactions between neighboring domains, and a stronger exothermic interaction process between DMAc and these groups occurs. In the white sample, it is likely that a stronger endothermic process is required to disrupt the more perfectly formed urea/urea interactions to then enable interactions with the solvent, DMAc.



**Figure 5** Isosteric heats of sorption of both clear and white spandex as a function of solvent concentration. The limiting value as the solvent concentration increases approaches the heat of vaporization of DMAc.

In the most extreme situation, access to unpaired ureas should be greatly reduced and sorption is expected to be concentrated in the nonpolar ether soft segment regions. The less attractive interactions between DMAc and the soft segments may lead to clustering as is seen with water in nonpolar environments. In the limit of high concentrations, an enthalpy of sorption equal to the heat of vaporization is observed due to clustering, since desorption amounts to removal of a penetrant from a liquidlike cluster. The tendency for the isosteric enthalpies for both the white and clear samples to approach this limit suggests that clustering may be occurring, but one would need to consider the form of the concentration-dependent diffusion coefficient at high DMAc activity to further investigate this issue.<sup>22</sup> A tendency for the diffusion coefficient to decrease somewhat with increasing concentration is generally taken as a strong indicator for clustering in cases where the sorption isotherms inflect upwardly as in the present system.

## SUMMARY

Significant differences were observed between sorption isotherms for DMAc/spandex solutions containing small amounts of TiO<sub>2</sub> as compared to otherwise identical solutions without the TiO<sub>2</sub>. The observed differences are consistent with the functioning of the TiO<sub>2</sub> particulate as heterogeneous nuclei that promote the hard segment domain assemblage. Isosteric enthalpy differences between the two samples are also consistent with this mechanism. Specifically, the tendency for more exothermic sorption to occur in the clear samples as opposed to the white samples can be rationalized in terms of more accessible polar groups for interaction with DMAc in the less perfectly assembled clear samples. The tendency for the isosteric enthalpy of sorption to approach the heat of vaporization of DMAc in an asymptotic manner, coupled with the upwardly inflecting sorption isotherm shapes, suggests that clustering of DMAc may be occurring at high activities. Unlike simple homopolymers, however, clustering may be suppressed by virtue of the polar urea groups that may be accessible to DMAc if the urea/urea interactions are disturbed sufficiently by DMAc. This issue of clustering can be best considered with the help of complementary DMAc mobility data that will be presented in a future part of this study.

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