

# Sorption of *N*-Butane, Propane, and Ethane in Ethylcellulose

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## Synopsis

The sorption of *n*-butane, propane, and ethane in ethylcellulose has been investigated between 0 and 200 mm Hg pressure over the temperature range from 30 to 70°C. Sorption isotherms of *n*-butane, propane, and ethane in ethylcellulose suggest that both Henry's law and the Langmuir forms of sorption, are operative. Sorption data were analyzed using the dual sorption model and sorption parameters determined. The sorption attributed to the Langmuir mode decreases as the temperature increases. This result indicates that the non-linear Langmuir mode of sorption is more characteristic of the glassy state than sorption represented by the Henry's law mode. It was found that sorption attributed to the Henry's law and Langmuir modes decreases as the molecular size of gaseous hydrocarbon penetrants decrease. In this study, the molecular size of gaseous molecule decreased as the gases studied changed from *n*-butane to propane to ethane. A correlation of the Henry's law constants for the solution of *n*-butane, propane, and ethane in ethylcellulose with the Lennard-Jones force constants,  $\epsilon/k$  at different temperatures was also determined. The temperature dependence of the Henry's law constants were correlated by a van't Hoff relationship and heats of sorption determined.

## INTRODUCTION

The sorption of gases in rubbery polymers often occurs by the process of ordinary dissolution and can be represented by Henry's law. At temperatures below the glass transition, a polymer matrix may contain microvoids or holes because of the immobilization and incomplete relaxation of polymer chains. Because of the complex nature of the glassy state, the equilibrium sorption of some gases may not follow Henry's law. The sorption of gases in glassy polymers has been visualized as dominated by two processes. One process is ordinary dissolution described by Henry's law, and the other process is concerned with the filling of microcavities or holes in the polymer matrix and is described by the Langmuir isotherm. The dual sorption theory<sup>1</sup> has been developed to describe sorption by these two modes. This theory describes the concentration of the sorbed penetrant to be the result of sorption by both the Henry's law and the Langmuir processes.

$$C = C_D + C_H \quad (1)$$

$$C = k_D P + \frac{C_H' b p}{1 + b p} \quad (2)$$

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where  $C$  is the total concentration of sorbed penetrant,  $C_D$  is the sorption of species described by Henry's law,  $C_H$  is the sorption in microvoids or holes described by the Langmuir isotherm,  $k_D$  is the Henry's law constant,  $C'_H$  is the microvoid saturation constant,  $b$  is the microvoid affinity constant, and  $p$  is the pressure. A number of studies<sup>2-8</sup> have used this theory to describe sorption in glassy polymers.

## EXPERIMENTAL

### Materials

Ethylcellulose used in this study was donated by the Dow Chemical Company and is designated standard Ethocel 10 cp. It contains 48–49.5 wt% ethoxy and is in the form of a white powder with a reported<sup>3</sup> glass transition temperature of about 123°C and a density of 1.13 g/cm<sup>3</sup>. Ethane, propane, and *n*-butane, the penetrant gases used in this work, were purchased from Air Products and Chemical Company. The purity of the *n*-butane and propane were 99.5%, and the purity of the ethane was 99%. The gases were used as received.

### Sample Preparation

Butyl acetate was used as the solvent in the preparation of ethylcellulose films. Ethylcellulose (1 g) was dissolved in 20 ml butyl acetate. After a period of 2 days to allow for complete dissolution, films were cast on a clean mercury surface and the solvent slowly evaporated away at room temperature. The films were then washed with water and vacuum dried several days to guarantee complete removal of the solvent. Cast films were clear and flexible.

### Sorption Experiment

The equilibrium sorption of gases were determined by a gravimetric method using a Cahn electromagnetic microbalance (Model RG). The sorption apparatus,<sup>9</sup> which incorporates the Cahn balance, is illustrated in Figure 1. Sorption results were found to be reproducible after samples were con-

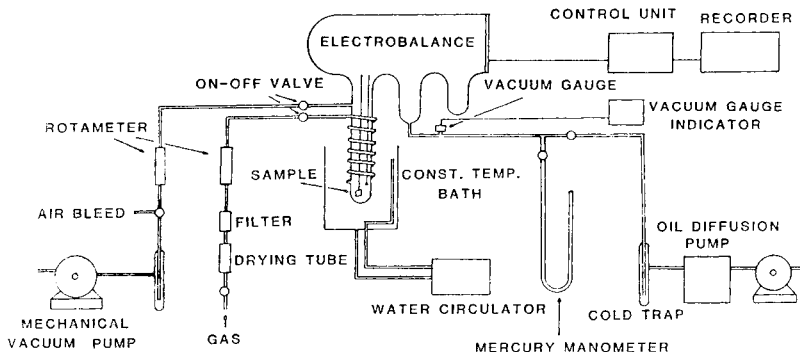


Fig. 1. Schematic diagram of sorption apparatus.

ditioned in the following manner. After the completion of vacuum degassing, ethylcellulose samples were exposed to *n*-butane gas for a sufficient period to allow equilibrium sorption to be reached at 30°C and a pressure of 300 mm Hg. At the end of this time, the temperature was increased to 70°C. Since the sorption capacity of ethylcellulose is less at the higher temperatures, desorption of *n*-butane took place until equilibrium was reached at 70°C and 300 mm Hg pressure. A high vacuum was then applied until desorption was complete, and the temperature was then reduced to 30°C.

When the calibration of the electrobalance was completed, the sorption experiment was begun by first suspending a sample in the balance. The system was then brought to a constant temperature and the sample degassed by applying a high vacuum. Degassing continued until there was no change in the weight of the sample. At the completion of the degassing the line to the vacuum pump was closed, one of the test gases was introduced into the system until the desired pressure was obtained, and then the system was sealed. The change in the weight of the sample was followed, and equilibrium sorption was considered to have been reached when the weight of the sample was constant for several hours. The valve to the gas line was then opened, and gas was introduced into the system until the higher pressure required for the next measurement was reached. Sorption of a gas was followed by recording the weight change with time at constant temperature until the new equilibrium condition was achieved. This process was continued until sufficient data for each sorption condition were collected. High vacuum was then applied, and the sample was degassed until it reached its original weight. The temperature was then changed, and equilibrium sorption experiments were repeated. The volume of the electrobalance container is very large in comparison with the sample volume, and the samples have low solubilities; therefore, there was practically no change in pressure due to gas sorption in the film sample during the experiment. Corrections were made for buoyancy effects.

A nonlinear least-squares regression analysis was used to determine the sorption parameters by obtaining the best fit of eq. (2) to all the experimental data.

## RESULTS AND DISCUSSION

### Sorption Isotherms

The solubilities of *n*-butane, propane, and ethane in ethylcellulose have been determined at 30, 40, 50, 60, and 70°C and at penetrant pressures up to 200 mm Hg. Sorption isotherms of *n*-butane, propane, and ethane in ethylcellulose are shown in Figures 2 through 4. The experimental data were analyzed according to the dual sorption model, and the sorption parameters for this model are presented in Table I. The solid lines in Figures 2 through 4 were calculated from eq. (2) by using the sorption parameters shown in Table I. The experimental points are in good agreement with the solid curves, indicating that the sorption of these gases in ethylcellulose is satisfactorily represented by the dual sorption model over the range of temperatures and pressures investigated.

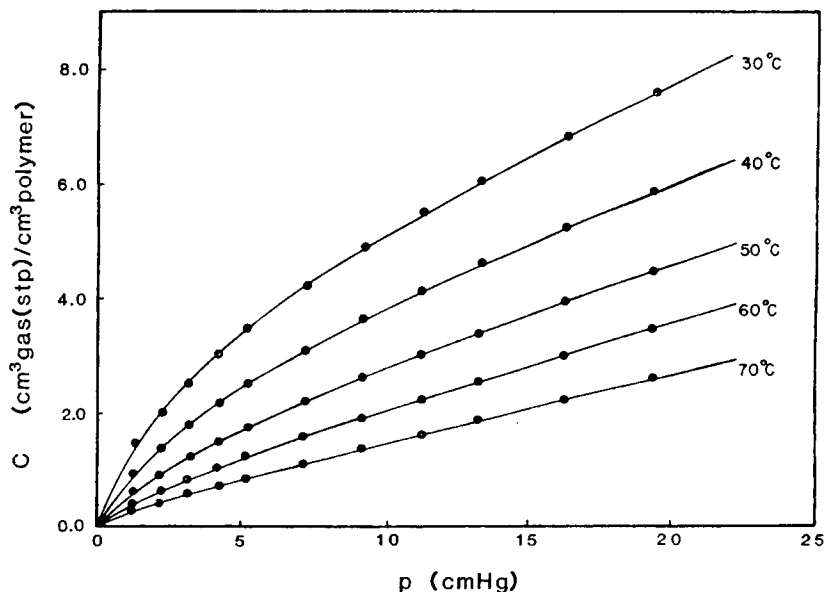


Fig. 2. *n*-Butane sorption isotherms in ethylcellulose at various temperatures.

The applicability of the Langmuir relation in describing sorption in microvoids can be tested by plotting  $1/C_H$  versus  $1/p$  as suggested by eq. (3).

$$\frac{1}{C_H} = \frac{1}{C'_H} + \frac{1}{C'_H p} \quad (3)$$

The solid lines in Figure 5 were calculated from Eq. (2) using the values of  $C'_H$  and  $b$  given in Table I. The points in Figure 5 were calculated from the pressure data using the inverse of eq. (1). The lines in Figures 2 through 5

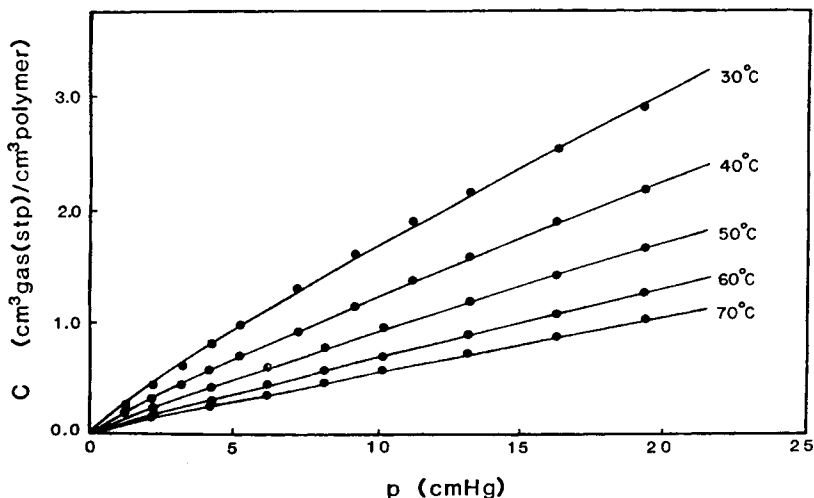


Fig. 3. Propane sorption isotherms in ethylcellulose at various temperatures.

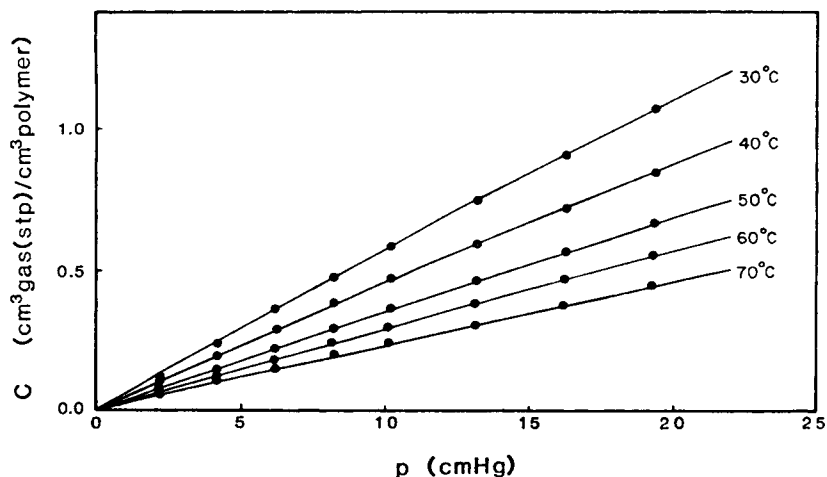


Fig. 4. Ethane sorption isotherms in ethylcellulose at various temperatures.

show that the experimentally determined points can be well predicted by eq. (2) by using the appropriate sorption parameters from Table I.

The dual sorption isotherms of *n*-butane, propane, and ethane in ethylcellulose are shown in Figures 6 through 8. The solid lines, which represent the Langmuir sorption isotherms, were calculated using the second term of eq. (1) with parameters from Table I. In these figures the sorption of gases in ethylcellulose is separated into contributions characteristic of each mode.

The saturation of Langmuir sorption sites is strongly dependent on the penetrant pressure. At high pressures the microvoids become saturated where  $bp \gg 1$ , and the Langmuir-type sorption reaches a limiting value

TABLE I  
Dual Sorption Parameters for *n*-Butane, Propane, and Ethane in Ethylcellulose  
at Various Temperatures<sup>a</sup>

	<i>T</i> (°C)	<i>k<sub>D</sub></i>	<i>C'<sub>H</sub></i>	<i>b</i>	<i>k</i>
<i>n</i> -Butane	30	0.2282	3.718	0.3128	5.096
	40	0.1884	2.650	0.2684	3.775
	50	0.1635	1.577	0.2645	2.551
	60	0.1439	0.809	0.3043	1.712
	70	0.1181	0.303	0.4251	1.305
Propane	30	0.1319	0.479	0.2914	1.058
	40	0.1012	0.295	0.2601	0.757
	50	0.0769	0.217	0.2347	0.661
	60	0.0613	0.096	0.3280	0.514
Ethane	30	0.0493	0.089	0.3267	0.588
	40	0.0476	0.348	0.0349	0.255
	50	0.0378	0.300	0.0307	0.244
	60	0.0295	0.299	0.0225	0.229
	70	0.0248	0.280	0.0179	0.202
	70	0.0199	0.250	0.0169	0.212

<sup>a</sup> *k* = cm<sup>3</sup> gas (STP)/cm<sup>3</sup> polymer (cm Hg). *C'<sub>H</sub>* = cm<sup>3</sup> gas (STP)/cm<sup>3</sup> polymer. *b* = (cm Hg)<sup>-1</sup>.

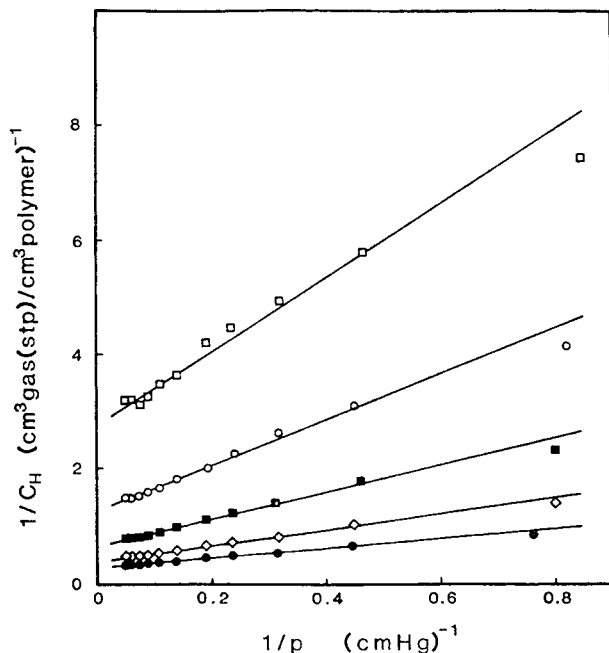


Fig. 5. Test of applicability of Langmuir equation for describing Langmuir-type sorption of *n*-butane in ethylcellulose at various temperatures; (●) 30°C; (◇) 40°C; (■) 50°C; (○) 60°C; (□) 70°C.

as the pressure becomes large. The dual sorption model assumes that microvoids that may be present in the glassy polymer disappear as the temperature is increased and as the glass transition temperature is approached.<sup>4</sup> The decrease in the Langmuir sorption capacity is directly related to the amount of unrelaxed polymer volume.<sup>4,9,10</sup> Figures 6 to 8 show the decrease of  $C_H$  with increasing temperature. In the case of sorption of *n*-butane in ethylcellulose by the Langmuir mode, the value of  $C_H$  of 3.145 cm<sup>3</sup> (STP)/cm<sup>3</sup> polymer at 30°C and 19.4 cm Hg pressure is reduced to 0.316 cm<sup>3</sup> (STP)/cm<sup>3</sup> polymer at 70°C and the same pressure. This 10-fold decrease in the Langmuir capacity can be attributed to a reduction in the number of Langmuir sorption sites as a result of increased chain mobility at the higher temperature as well as increased chain mobility due to the plasticization effect of *n*-butane. As the gas dissolves, it plasticizes the polymer and reduces the glass transition temperature. Since the Henry's law constant of *n*-butane is greater than that for propane and ethane, the *n*-butane-ethylcellulose system may have a lower glass transition temperature than the propane or ethane-ethylcellulose systems. The sharp decrease in the value of  $C_H$  may be related to the lowering of the glass transition temperature for the *n*-butane-ethylcellulose system.

### Henry's Law Constants

The Henry's law constants presented in Table I are in good agreement with reported values. Hsieh<sup>11</sup> reported that the gravimetrically determined  $k_D$  values are 0.2658 cm<sup>3</sup> gas(STP)/cm<sup>3</sup> copolymer-cm Hg for *n*-butane,

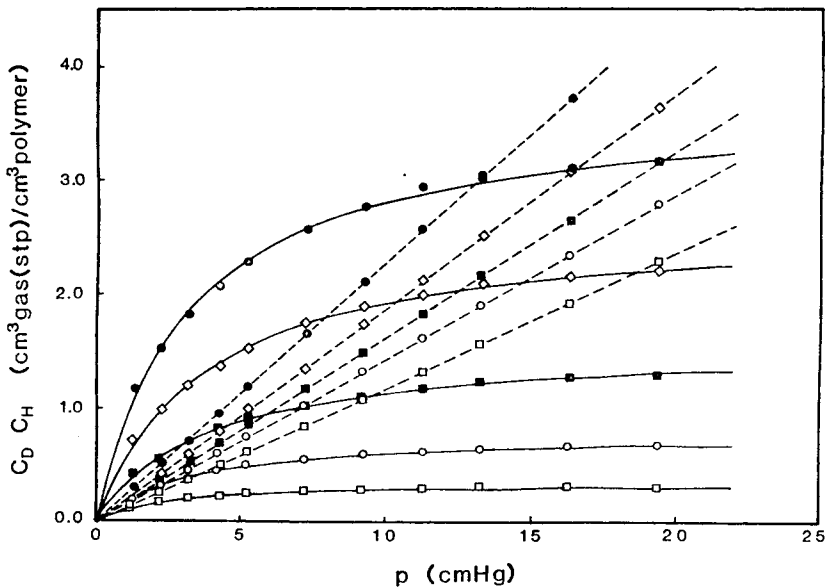


Fig. 6. Dual sorption isotherms of  $n$ -butane in ethylcellulose at various temperatures; (●) 30°C; (◇) 40°C; (■) 50°C; (○) 60°C; (□) 70°C; (- - -) Henry's law; (—) Langmuir-type sorption.

0.1263  $\text{cm}^3 \text{ gas(STP)/cm}^3 \text{ polymer-cm Hg}$  for propane, and 0.0484  $\text{cm}^3 \text{ gas(STP)/cm}^3 \text{ polymer-cm Hg}$  for ethane-ethylcellulose at 25°C. In this study, the values of  $k_D$  at 30°C were found to be 0.2282  $\text{cm}^3 \text{ gas(STP)/cm}^3 \text{ polymer-cm Hg}$  for  $n$ -butane, 0.1319  $\text{cm}^3 \text{ gas(STP)/cm}^3 \text{ polymer-cm Hg}$  for propane, and 0.04758  $\text{cm}^3 \text{ gas(STP)/cm}^3 \text{ polymer-cm Hg}$  for ethane. Sorption and transport data reported by Barrer et al.<sup>12</sup> for  $n$ -butane in ethyl-

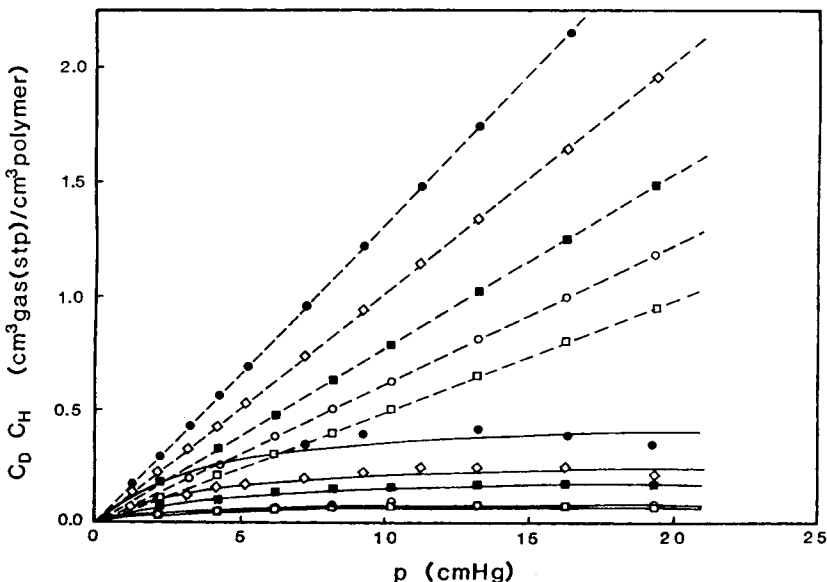


Fig. 7. Dual sorption isotherms of propane in ethylcellulose at various temperatures; (●) 30°C; (◇) 40°C; (■) 50°C; (○) 60°C; (□) 70°C; (- - -) Henry's law; (—) Langmuir-type sorption.

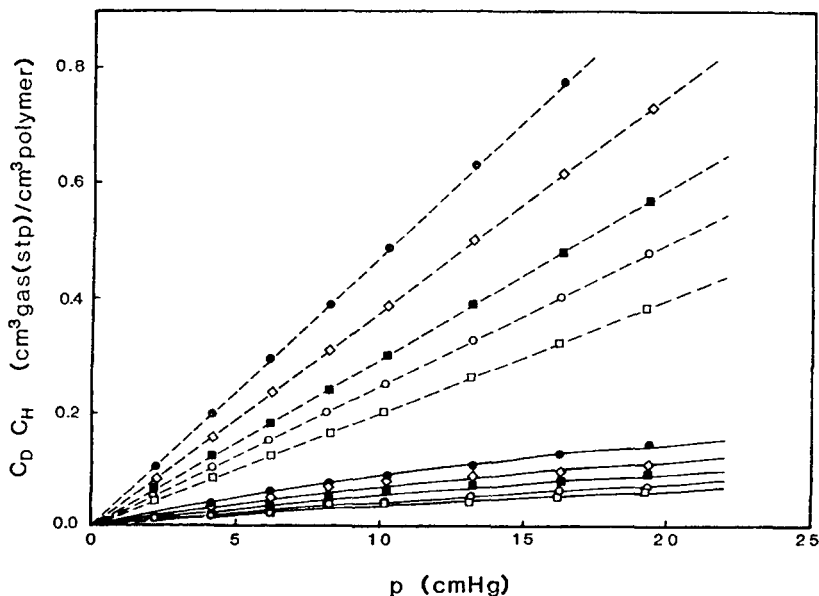


Fig. 8. Dual sorption isotherms of ethane in ethylcellulose at various temperatures; (●) 30°C; (◇) 40°C; (■) 50°C; (○) 60°C; (□) 70°C; (- -) Henry's law; (—) Langmuir-type sorption.

cellulose have been analyzed according to the dual sorption model by Chan et al.<sup>3</sup> Their reported values for  $k_D$  at 30.5°C is about 0.17 cm<sup>3</sup>(STP)/cm<sup>3</sup> polymer-cm Hg.

The temperature dependence of the Henry's law constant is given by the van't Hoff relation as

$$k_D = k_0 \exp\left(-\frac{\Delta H_D}{RT}\right) \quad (4)$$

where  $\Delta H_D$  is the heat of ordinary dissolution. van't Hoff plots for the gases studied are shown in Figure 9. Correlation of the Henry's law constants  $k_D$  for *n*-butane, propane, and ethane with  $\epsilon/k$  at five different temperatures are shown in Figures 5 through 9. An exponential relationship between the gas-polymer interaction and ordinary dissolution is indicated.

### Microvoid Saturation Constant

The unrelaxed volume of the glassy polymer decreases as the temperature increases and approaches zero at the glass transition temperature. Studies have shown that since the Langmuir form of sorption takes place within the unrelaxed polymer volume, the microvoid saturation constant  $C'_H$  is independent of temperature.<sup>4,6,10,13</sup>

A model proposed by Pace and Daytner<sup>14</sup> for the sorption of gases in



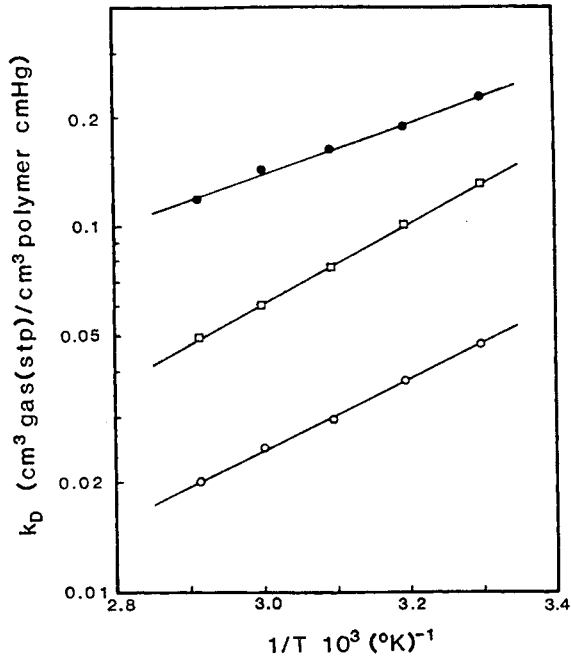


Fig. 9. van't Hoff plots of Henry's law constants in ethylcellulose; (●) *n*-butane; (□) propane; (○) ethane.

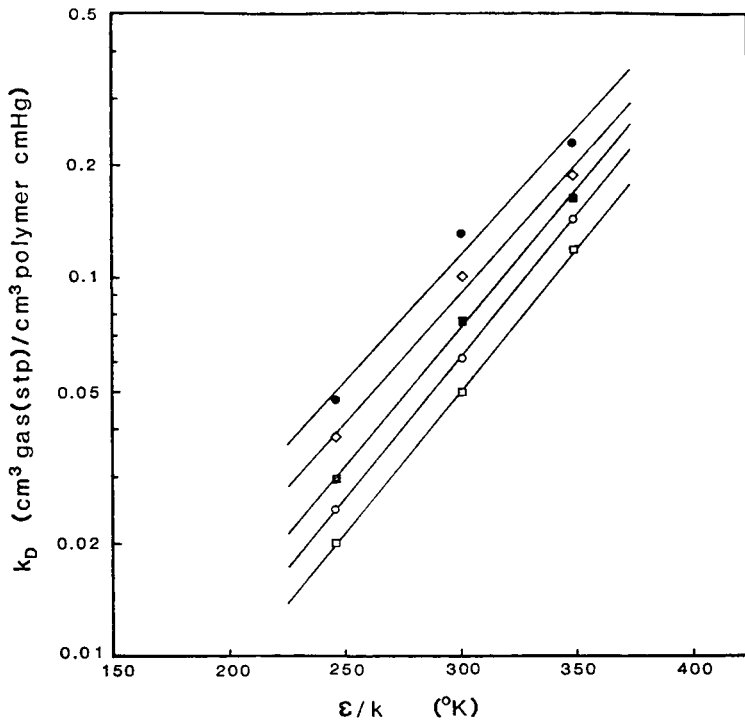


Fig. 10. Correlation of Henry's law constants with Lennard-Jones force constants; (●) 30°C; (◇) 40°C; (■) 50°C; (○) 60°C; (□) 70°C.

glassy polymers assumes that, below the glass transition temperature, the microvoid population is constant and the value of  $C'_H$  is independent of temperature. They related the change in the value of  $C'_H$  to the relaxation and disappearance of some of the microvoids as the result of the plasticization effect of the Henry's law species.

The temperature dependence of  $C'_H$  for *n*-butane is shown in Figure 11. The composite parameter  $K = C'_H b / k_D$ , which is the ratio of the quantity of gas absorbed in the Langmuir mode to the gas dissolved at a low pressure, becomes zero at the glass transition temperature. The temperature dependence of  $K$  is also presented in Figure 12. Within the temperature limits of this study it is difficult to conclude from examining the data shown in Figure 12 that  $C'_H$  becomes zero at the glass transition temperature, 123°C. The presence of highly soluble gas plasticizes the polymer and likely reduces the glass transition temperature for the *n*-butane-ethylcellulose system. The extrapolation of the data in Figure 12 may result in their values approaching zero around the glass transition temperature.

### Microvoid Affinity Constant

The microvoid affinity constant  $b$  represents the ratio of the rate constants for sorption and desorption of penetrant in the microvoids. The magnitude of  $b$  depends on the Lennard-Jones force constant  $\epsilon/k$  of the penetrant gas, and the quantity of gas sorbed in the microvoids is proportional to the specific gas-polymer interaction. For large values of  $\epsilon/k$ , the microvoids become saturated at low pressures and this results in a large value for  $b$ . The temperature dependence of  $b$  is given by the following van't Hoff relation.<sup>15</sup>

$$b = b_0 \exp\left(-\frac{\Delta H_b}{RT}\right) \quad (5)$$

where  $\Delta H_b$  is the enthalpy associated with the microvoid filling process. Plots of data for  $\ln b$  versus  $1/T$  for the three gases studied are shown in Figure 13. The values of  $b$  for ethane have the expected relationship between 30 and 70°C. Although the values of  $b$  for both *n*-butane and propane decrease linearly between 30 and 50°C, they show a sharp increase between 60 and 70°C. Since a high value of  $b$  is an indication of the saturation of microvoids at lower pressures, this behavior for *n*-butane and propane sorption above 50°C may be the result of structural changes in ethylcellulose due to the plasticizing effect of the penetrant gases. Pace and Datyner<sup>16</sup> attribute "the erratic temperature dependency" of the value of  $b$  in their work to the relaxation of microvoids as a result of the plasticizing effect of the penetrant gas, which is dependent on both the temperature and the penetrant gas concentration. Plasticization can change the microvoid population and result in a deviation of the Langmuir sorption parameters from

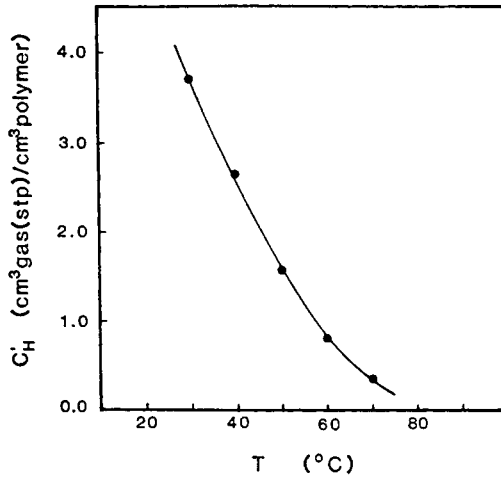


Fig. 11. Temperature dependence of microvoid saturation constant of *n*-butane in ethylcellulose.

the expected relationship. At low concentrations of penetrant the plasticization effect should be minimized.

### Heats of Sorption

At low pressures, eq. (2) reduces to

$$C = (k_D + C'_H b)p \quad (6)$$

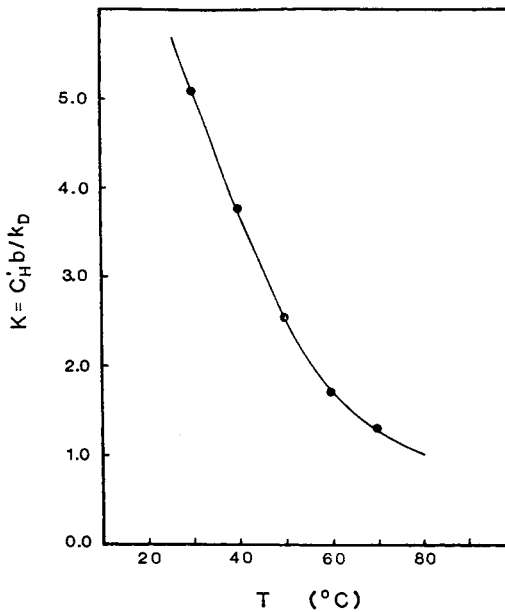


Fig. 12. Temperature dependence of composite sorption parameter *K* for ethylcellulose *n*-butane.

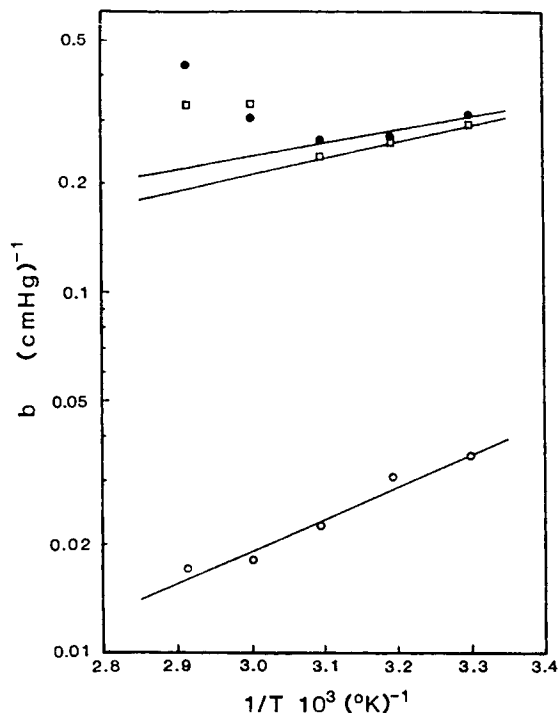


Fig. 13. van't Hoff plots of microvoid affinity constants in ethylcellulose; (●) *n*-butane; (□) propane; (○) ethane.

where  $k_D + C'_H b = k$  is the apparent solubility coefficient. The value of  $\Delta H_S$ ; the overall heat of sorption, is given by

$$\Delta H_S = -R \frac{\delta \ln (k_D + C'_H b)}{\delta(1/T)} \quad (7)$$

when both processes contribute to the sorption. If  $C'_H b \gg k_D$ , the microvoid filling process is predominant and eq. (7) takes the form

$$\Delta H_H = -R \frac{\delta \ln (C'_H b)}{\delta(1/T)} \quad (8)$$

where  $\Delta H_H$  is the apparent heat of sorption by microvoid filling. Figure 14 shows the van't Hoff plot of the  $\ln C'_H b$  versus  $1/T$  for *n*-butane, propane, and ethane. The van't Hoff plot of  $k$  is shown in Figure 15. The heat values for  $\Delta H_D$ ,  $\Delta H_b$ ,  $\Delta H_S$ , and  $\Delta H_H$  are given in Table II.

Ordinary solution involves both the condensation of the gas and the mixing of the condensed gas with the polymer. Mixing of the gas with the polymer requires chain displacement and formation of the microvoids to sorb the condensed gas. From a thermodynamic point of view, condensation is a exothermic process and mixing is an endothermic process. The heat of

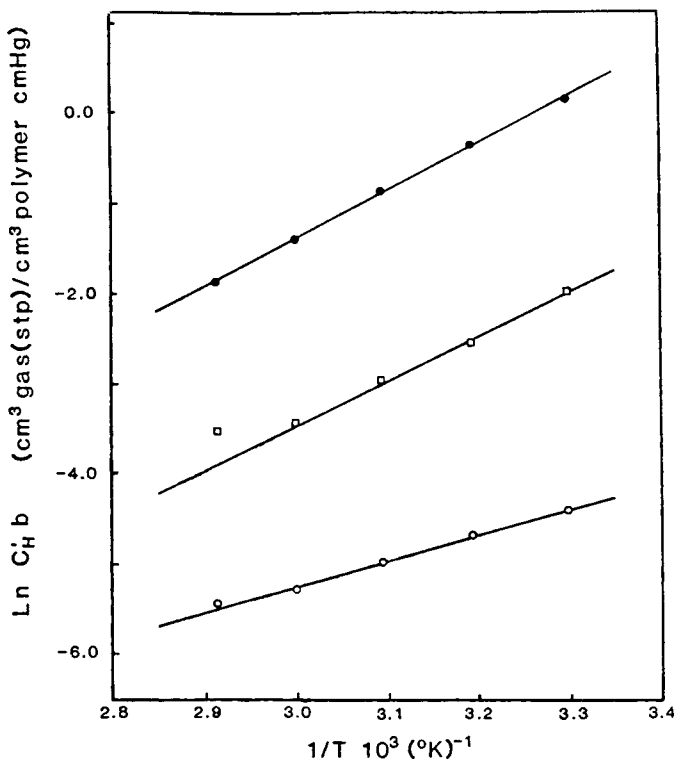


Fig. 14. van't Hoff plots of Langmuir sorption parameters in ethylcellulose; (●) *n*-butane; (□) propane; (○) ethane.

solution for low-molecular-weight hydrocarbons is determined principally by the heat of condensation.

Values shown in Table II show that the apparent heat of sorption by microvoid filling  $\Delta H_H$  is more exothermic than the overall heat of sorption  $\Delta H_S$  for *n*-butane, propane, and ethane. These results are consistent with the dual sorption model.

Using the sorption isotherms of *n*-butane, propane, and ethane from Figures 2 through 4, the solubility coefficients at different pressures and temperatures for constant values of concentration were determined and the isothermic heats of sorption were determined using the equation

$$\Delta H_I = -R \left\{ \frac{\delta \ln [(k_D + C'_H b)/(1 + bp)]}{\delta(1/T)} \right\}_c \quad (9)$$

The variation of  $\Delta H_I$  with the concentration of *n*-butane, propane, and ethane are shown in Figures 16 through 18. The isosteric heat curves of *n*-butane and propane indicate that  $\Delta H_I$  becomes more exothermic at low concentrations at which the microvoid filling process is predominate. As the concentration increases, the contribution of  $\Delta H_H$  to  $\Delta H_I$  becomes less and  $\Delta H_I$  tends toward the less exothermic  $\Delta H_D$ . These results are consistent with other reported systems.<sup>9,15,17</sup>

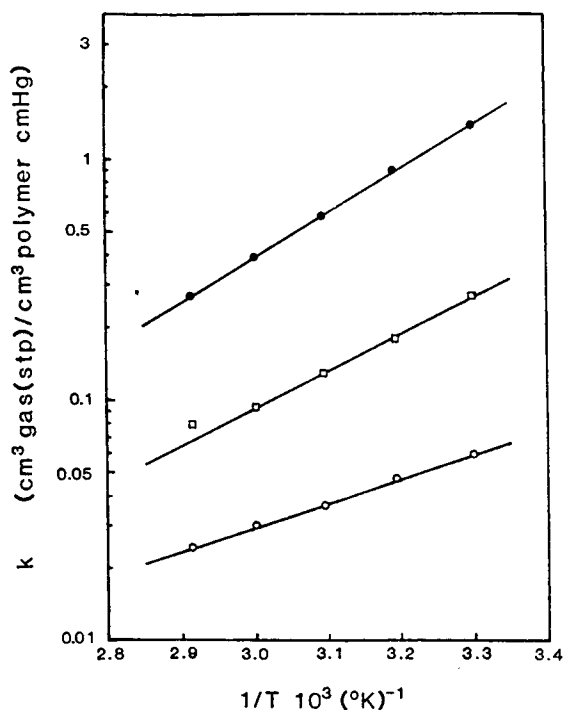


Fig. 15. van't Hoff plots of apparent solubility coefficients in ethylcellulose; (●) *n*-butane; (□) propane; (○) ethane.

## CONCLUSIONS

This work has shown that the dual sorption model provides a satisfactory description of the sorption of *n*-butane, propane, and ethane in ethylcellulose. The magnitude of Langmuir-type sorption for *n*-butane in ethylcellulose is greater than that for propane or ethane because of plasticization and swelling of the polymer by *n*-butane. The magnitude of the Henry's law constant and the composite dual sorption parameter *K* decrease as the penetrant gas solubility decreases.

The temperature dependence of both the Langmuir-type sorption and the microvoid saturation constant are consistent with the view that they are associated with the unrelaxed volume of ethylcellulose. As the temperature

TABLE II  
Heat of Sorption in Ethylcellulose<sup>a</sup>

	$\Delta H_D$	$\Delta H_b$	$\Delta H_s$	$\Delta H_H$
<i>n</i> -Butane	-3.27	-1.65	-8.46	-10.53
Propane	-5.10	-2.10	-7.13	-9.78
Ethane	-4.46	-4.12	-4.68	-5.63

<sup>a</sup> Values are in kilocalories per mole.

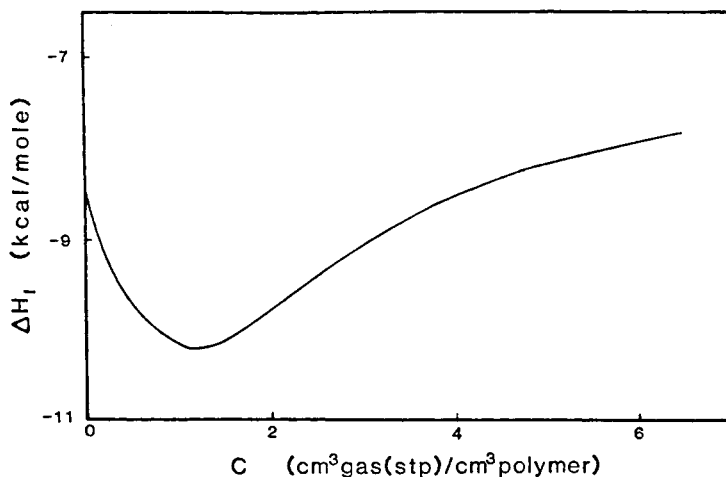


Fig. 16. Isosteric enthalpy of sorption for *n*-butane in ethylcellulose.

increases, the greater segmental mobility of polymer chains reduces the free volume of glassy ethylcellulose. This reduction in free volume is substantiated by a decrease in the quantity of Langmuir-type sorption and a decrease in the magnitude of the microvoid saturation constant. This is also confirmed by the temperature dependence of  $K$ . It is not possible from this work to verify the notion that the Langmuir-type sorption and the microvoid saturation constants always become zero at the glass transition temperature.

The results indicate that the heat of microvoid filling  $\Delta H_b$  is less exothermic than the heat of ordinary solution  $\Delta H_D$ . The apparent heat of microvoid filling  $\Delta H_H$  may be used to describe the heat of sorption in the

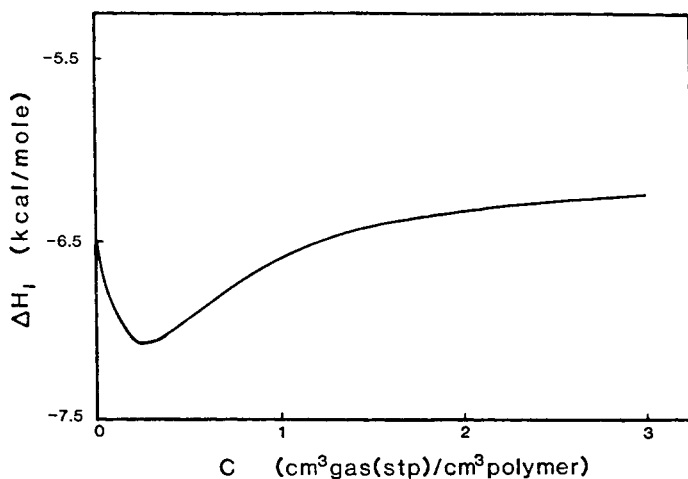


Fig. 17. Isosteric enthalpy of sorption for propane in ethylcellulose.

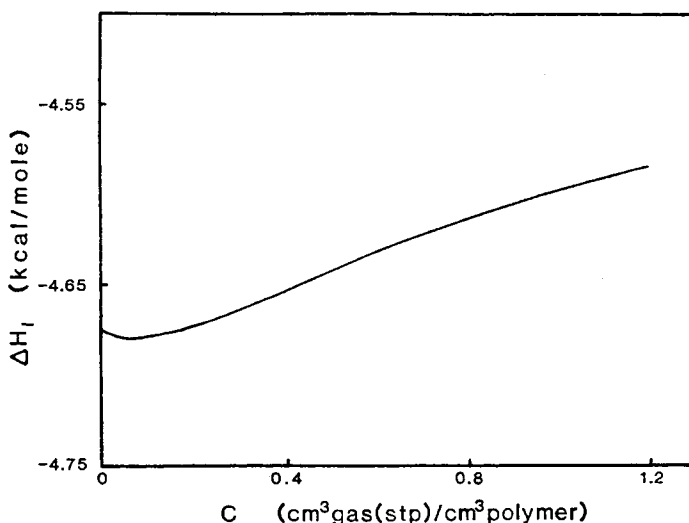


Fig. 18. Isosteric enthalpy of sorption for ethane in ethylcellulose.

microvoids since it is more exothermic than the heat of ordinary solution, and this is consistent with the thermodynamic interpretation of the heat of sorption.

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