Diffusibility and Solubility of Gases in Ethylcellulose and Nitrocellulose

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INTRODUCTION

Diffusion of molecules in a polymer film, while affected by temperature and pressure, depends on the structure of the polymer film and on the physical properties of penetrants. The dependence of the diffusion constant D on the size of the penetrating molecule has been shown,[1] and the linear relationship between log D and the square of the extrapolated diameter of penetrant at infinite temperature d_∞ has been demonstrated.[2,3] The extrapolated diameter was found to correlate well with the diffusion coefficient in many cases. Michaels and Bixler[4] have recently shown a linear correlation of the logarithm of a reduced diffusion constant D/d^2 with the reduced molecular diameter $d - (\varphi^{1/2}/2)$. Here d is the diameter of the gas molecule and φ is the free volume per unit length of a methylene group measured along the chain axis in polyethylene, or $\varphi^{1/2}/2$ is approximately equal to the mean unoccupied distance between two chain segments.

A correlation between the diffusion constant and the physical properties of a penetrant may be derived in various ways. The kinetic theory of gases shows that

$$D = {}^1\!/_3\lambda\bar{w} \tag{1}$$

where D is the diffusion coefficient, λ is the mean free path, and $\bar{w}$ is the root-mean-square velocity. At constant temperature, $\bar{w}$ and λ are functions of the molecular weight M, i.e., $\bar{w} \propto M^{1/2}$ and $\lambda \propto M^{-1/2}$. Hence, D is reduced to a function of molecular weight.

The same relationship would also result from a consideration of the permeating gas molecule in Brownian motion inside the macromolecular film. The diffusion coefficient is given by

$$D = RT/6\pi\eta r N \tag{2}$$

where R is the gas constant, T is the absolute temperature, η is the viscosity of the medium, r is the mean radius of the permeating molecule, N is Avogadro's number, and D is the diffusion coefficient. According to the kinetic theory, the viscosity of a gas can be expressed as

$$\eta = (M/3)w\lambda c \tag{3}$$

where w, λ, c, and M are the velocity, mean free path, concentration, and molecular weight of a gas, respectively. At constant temperature, w and λ are functions of the molecular weight only. Therefore, at constant temperatures, viscosity is a function of molecular weight. Since r is also related to molecular weight, eq. (2) can be reduced to

$$D = f(M) \tag{4}$$

It is also well known that the Schmidt number s_c for gases is nearly constant. The Schmidt number for gases is defined as

$$s_c = \eta/\rho D \tag{5}$$

where ρ is the density of the gas. Therefore D is equal to a constant times (η/ρ). Thus eq. (5) can also be reduced to eq. (4).

Let us assume that eq. (4) can be written as

$$D = bM^a \tag{6}$$

where a and b are functions of both film structure and temperature and are constant for a particular film at a fixed temperature. Log D should be a linear function of log M.

Fick's law of diffusion has been found to apply in the flow of gases through polymer films.[5,6] The solubility of gas in a polymer has also been shown to contribute significantly to the permeability. The roles played by solubility and diffusion have been discussed by Van Amerongen[6] from the permeability of small molecules in rubberlike elastomers[7] and of water and nitrogen in polyethylene films. McCall and Schlichter[3] have also discussed the effects of solubility and diffusion from permeability data for hydrocarbons in polyethylene films.

A combination of Fick's law of diffusion and Henry's law (the solubility of a gas in a polymer is proportional to the pressure) will give

$$P = DS \tag{7}$$

where P is the permeability constant, i.e., the flux rate per unit pressure gradient, and S is the solubility constant.

From eqs. (6) and (7), it can be shown that

$$\log P = \log D + \log S = a \log M + \log b + \log S \tag{8}$$

Therefore, a plot of log P versus log M should be linear if the solubility constant either changes linearly with, or is independent of the change in molecular weight. Equation (8) was tested with data determined by Müller,[9] and the results indicated the correctness of the approximations used in obtaining eq. (6).

The test with Müller's data also indicated that, for noble gases, P is approximately equal to D and diffusion predominates in the process.

The permeability data of Pinsky[10] (for polyethylene films with alcohols and hydrocarbons) also show the general tendency of permeability to decrease with an increase of molecular weight.

Equation (8) was further tested by the permeability data of low molecular weight paraffin hydrocarbons determined by Brandt.[2] The same linear relationship was obtained.

The approximation that the molecular cross-sectional area is related to molecular weight seems valid for the molecules of similar shapes. In order to study the effect of the shape of the penetrating molecules on the diffusion coefficients, the permeabilities of polar and nonpolar inorganic molecules and of some low molecular weight hydrocarbons in ethylcellulose and nitrocellulose films were determined.

It is desirable to relate the solubility of a molecule to its thermodynamic properties. The Lennard-Jones potential has been widely used for the calculation of the properties of matter in the gas, liquid, and solid states. Jolley and Hildebrand[11] have shown that, for different gases in the same solvent, log X_2 (X_2 being the mole fraction of the gas) increases linearly with an increase in the Lennard-Jones force constants, ϵ/k, of the gases. This relationship was applied to gases in liquid solvents. From the solubility of various gases in polyethylene, Michaels and Bixler[12] have recently demonstrated that the solubility constants increase linearly with an increase of the Lennard-Jones force constants when the solubility of gases is expressed as concentration on a volume basis.

In this work, the solubility constants have been determined for various gases in ethylcellulose and nitrocellulose, not only for the purpose of calculating diffusion coefficients, but also for finding a correlation with the Lennard-Jones force constants.

EXPERIMENTAL

Materials

Anhydrous ammonia, argon, n-butane, carbon dioxide, ethane, helium, nitrogen, oxygen, propane, and sulfur dioxide were obtained from The Matheson Company. The minimum purity of all gases was 99.5%, except for ethane which was 99%. The gases were used directly without further purification. n-Pentane and n-hexane were supplied by the Matheson, Coleman and Bell Company and were distilled directly into the system.

Dissolved gases in the distilled water used in the experiments were removed before distilling into the system. This was accomplished by freeze-evacuate-thaw cycles.

Both ethylcellulose (T 50, viscosity 44, ethoxy 49.5%) and nitrocellulose (RS 60–80 sec., viscosity 60, butyl alcohol 30%), which were obtained from The Hercules Powder Company, were vacuum dried at 40°C. before use. Methyl ethyl ketone, CP grade, was used to dissolve the polymers. The films were prepared by casting the solutions, which were made by dissolving the polymer in methyl ethyl ketone, onto a glass plate. The films were aged at 25°C. for at least a month and then pumped in high vacuum for a minimum of two weeks before any determinations were started. Although

complete removal of any solvent from the films is very difficult, it is believed that any solvent effect was reduced to a minimum.

The crystallinity of both the cast films determined by x-ray diffusion showed very little crystalline structure, if any. The densities of the cast films of ethylcellulose and nitrocellulose were determined by weighing in air and in water and were found to be 1.10 and 1.46 g./cm.³, respectively.

Gas Permeability

The gas permeability was determined by the high vacuum technique originally used by Doty, Aikens, and Mark.[13] The apparatus was evacuated before introducing the penetrant into the upper compartment of the permeability cell. This cell, which was made from stainless steel, held the polymer film to be studied. The rate of pressure build-up in the downstream compartment of known volume was measured by a McLeod gauge. The pressure in the upper compartment was measured by a conventional mercury manometer. The pressure drop across the film was constant during the determination.

The permeability constant P, which is the rate of the film resistance to molecular transmission, was computed from the equation,

$$P = (VCh^2\ 273/760\ T)B/\Delta pat \qquad (9)$$

where P is the permeability constant in cc. (STP) $\times$ mm./sec. $\times$ cm.² $\times$ cm. Hg, V is the volume of the downstream compartment in cubic centimeters, C is the McLeod gauge constant, h is the distance between the top of the capillary of the McLeod gauge and the top of the mercury column in the gauge, T is the room temperature (298 $\pm$ 0.5°K.), B is the thickness of the film in millimeters, Δp is the pressure difference across the film in centimeters of Hg, a is the area of the film subjected to transmission in square centimeters, and t is the time in seconds.

The main experimental error in the measurement of permeability constants would likely arise from the lack of uniformity of the film thickness of the different samples. However, since the same film was used for the measurements with all of the gases and vapors, this uncertainty was minimized.

The permeability constants of water vapor were determined by means of a conventional Payne cup.

A pressure difference of 5–6 cm. Hg was used throughout most of the determinations. This low pressure was chosen because the same pressure range had to be used for the solubility constant determinations, and it was believed that Henry's law would more nearly be obeyed at low pressures than at high pressures.

Solubility Constants

The solubility constants were determined from equilibrium sorption and the operation of the apparatus was exactly similar to that for adsorption isotherms.
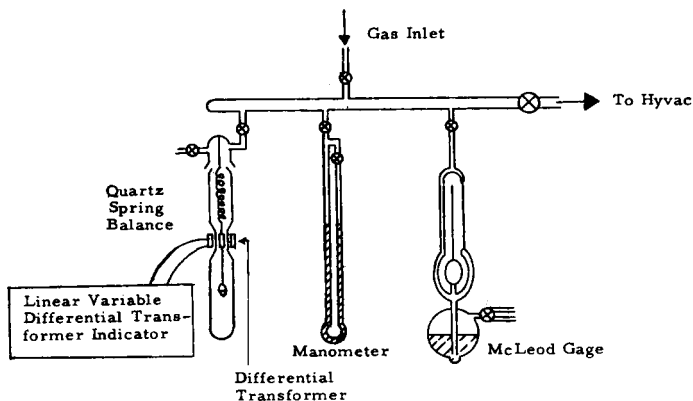
Fig. 1. Gravimetric gas adsorption apparatus.

The volumetric adsorption apparatus was a conventional one for determining adsorption isotherms. Gravimetric sorption isotherms were determined with a quartz helix microbalance as shown in Figure 1. The change in elongation of the quartz helix was detected by a linear variable differential transformer, Type 060 SLB (Schaevitz Engineering, New Jersey), and was amplified and read by means of a linear variable differential transformer indicator, Model 300B (Daytronic Corporation, Dayton, Ohio). A weight of 0.19 μg. could be measured by the balance when the quartz helix sensitivity was 1 g./cm. An automatic recorder was connected directly to the transformer indicator. Adaptation of the linear variable differential transformer to the microbalance was reported by Klevens and co-workers.[14]

A reference point was taken at the time when the adsorbate was introduced into the adsorption chamber; therefore, corrections for the buoyancy and adsorption of the adsorbate, etc., on the helix were not made.

The adsorption measurements were all carried out at 25°C. Both gravimetric and volumetric methods were used to check the data. When the glass apparatus or the stopcock grease adsorbed the adsorbate, data from the gravimetric method alone were used.

Diffusion Coefficients

Because the films used for the permeability measurements were very thin, the diffusion coefficients D were not measured directly by the time lag method,[13] but were computed by means of eq. (7), by using the experimentally found permeability constants P and solubility constants S. This approach is based on the findings of Michaels and Parker[15] and Michaels and Bixler.[12] According to them, solubility constants determined by equilibrium sorption measurements employing independent measurements of P and D for various gases and vapors in polyethylene were identical to those calculated by means of eq. (7).

TABLE I

Diffusion, Solubility and Permeability Constants of Gases for Ethylcellulose Films at 25°C. Density of the Film = 1.10

Gas	Pressure difference Δp, cm. Hg	Permeability constant P, cm.³ mm./sec. cm.² cm. Hg $\times 10^9$	Solubility constant S, cc. (STP)/cc. cm. Hg		Diffusion coefficient[a] D, cm.²/sec. $\times 10^{10}$	
			Volumetric[b]	Gravimetric[c]	Volumetric[b]	Gravimetric[c]
He	6.025	53.40	—	0.0024	—	22,066.0
N_2	4.490	4.43	0.0021	0.0019	2109.0	2331.0
O_2	4.845	14.70	0.0024	0.0023	6074.0	6391.0
A	5.08	10.20	0.0026	0.0025	3863.0	4032.0
CO_2	5.86	113.0	0.0207	0.0200	5459.0	5650.0
SO_2	5.655	264.0	0.4978	0.3596	530.0	734.0
NH_3	4.58	705.0	0.605	0.484	1165.0	1456.0
H_2O	2.26	8930.0	—	31.24	—	286.0
C_2H_6	5.09	9.2	0.0748	0.0484	123.0	190.0
C_3H_8	5.08	3.70	0.1534	0.1263	24.1	29.3
$n\text{-}C_4H_{10}$	4.51	3.87	0.3887	0.2655	9.9	14.6
$n\text{-}C_5H_{12}$	4.52	3.70	0.9426	0.2674	3.9	13.8
$n\text{-}C_6H_{14}$	4.10	7.66	2.4404	0.6165	3.1	12.4

[a] Calculated from the equation, $P = 10\ DS$.
[b] From the volumetric adsorption method.
[c] From the gravimetric adsorption method.

TABLE II

Diffusion, Solubility and Permeability Constants of Gases for Nitrocellulose Films at 25°C. Density for the Film = 1.46

Gas	Pressure difference Δp, cm. Hg	Permeability constant P, cm.³ mm./ sec. cm.² cm. Hg × 10⁹	Solubility constant S, cc. (STP)/cc. cm. Hg		Diffusion coefficient[a] D cm.²/sec. × 10¹⁰	
			Volumetric[b]	Gravimetric[c]	Volumetric[b]	Gravimetric[c]
He	4.68	6.9	—	0.0016	—	4312.0
N_2	5.21	0.116	0.0009	0.0006	129.0	193.0
O_2	4.995	1.95	0.0019	0.0013	1026.0	1500.0
A	5.15	0.11	0.0016	0.0014	68.7	75.3
CO_2	4.567	2.12	0.0131	0.0096	162.0	221.0
SO_2	4.442	1.76	0.2215	0.0977	7.9	18.0
NH_3	4.04	57.1	1.2359	0.7265	46.2	78.6
H_2O	2.195	6295.0	—	24.04	—	262.0
C_2H_4	4.92	0.063	0.0533	0.0483	1.18	1.30
C_2H_6	4.57	0.0084	0.0534	0.0394	0.16	0.21
$n\text{-}C_4H_{10}$	4.34	~0.0	0.0248	0.0147	0.0	0.0

[a] Calculated from the equation, $P = 10\ DS$.
[b] From the volumetric adsorption method.
[c] From the gravimetric adsorption method.

RESULTS AND DISCUSSION

Permeability

Permeability constants computed from eq. (9) and gas pressures at which the permeability determinations were made are presented in Tables I and II for the ethylcellulose and nitrocellulose films, respectively.

It will be noticed that the permeability of ethylcellulose to the gases determined is higher than that of nitrocellulose. It is also interesting to notice that nitrocellulose is practically impermeable to n-butane. Therefore, measurements on hydrocarbons higher than n-butane in the homologous series were not deemed necessary for nitrocellulose.

Since the same piece of film was used for all of the gas permeability measurements, it is possible that some penetrants might have been chem-
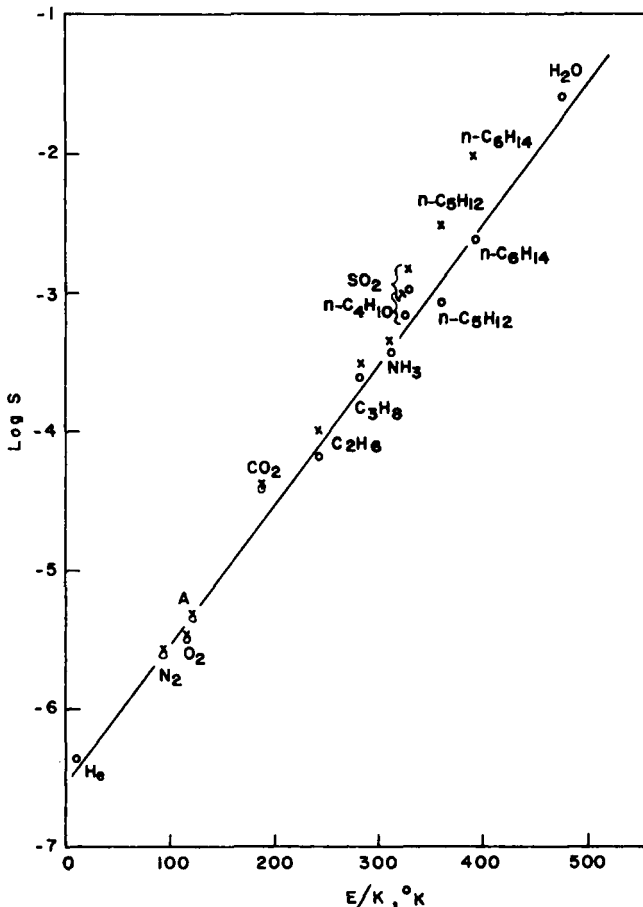

Fig. 2. Solubility of gases and vapors in ethylcellulose vs. Lennard-Jones force constants: (O) gravimetric adsorption; (X) volumetric adsorption.
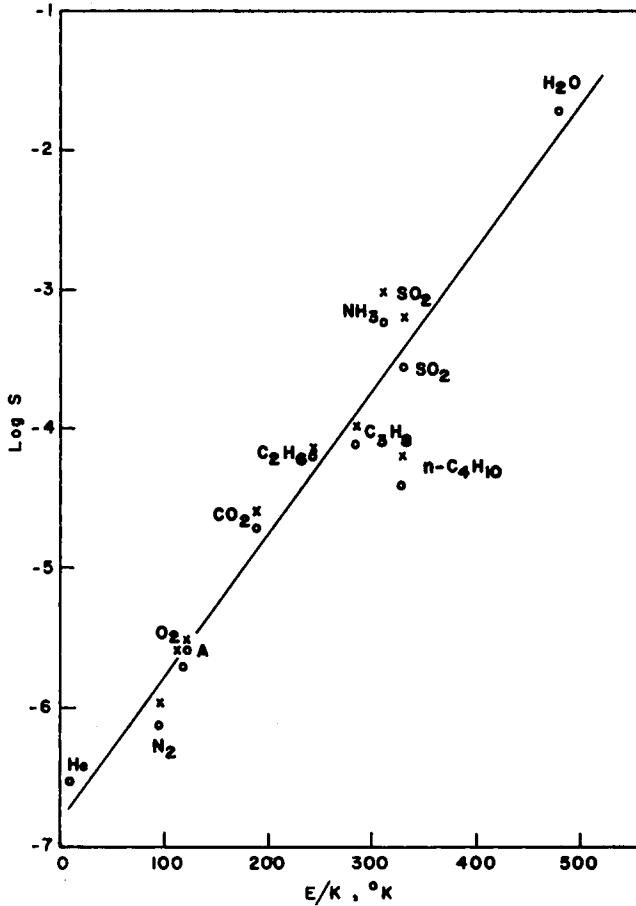
Fig. 3. Solubility of gases and vapors in nitrocellulose vs. Lennard-Jones force constants:
(O) gravimetric adsorption; (X) volumetric adsorption.

isorbed in the film and thus altered the film structure, affecting subsequent determinations. However, repeated experiments with the gases in the reverse order showed, within experimental errors, the same results as the first measurements.

Solubility

Solubility constants (in cubic centimeters of adsorbate per cubic centimeter adsorbent) determined from both gravimetric and volumetric methods are listed in Tables I and II for the ethylcellulose and nitrocellulose films, respectively.

In general, solubilities determined by gravimetric and volumetric methods are in good agreement. Solubility data determined for sulfur dioxide and the hydrocarbons, especially the higher molecular weight ones, by the volumetric method were higher than those obtained by the gravi-

metric method.   These differences might be attributed to the adsorption of the gases by the stopcock grease (Apiezon N) present in the apparatus.

The adsorption isotherms are not linear for all of the gases investigated. Since the solubility is not linear with respect to pressure in some cases, solubility data were taken from the adsorption isotherms at the corresponding pressure used during the permeability determinations.

In the case of ammonia on nitrocellulose, strong absorption was observed. This high apparent adsorption could be attributed to reaction with the free acid which was present in the adsorbent.   Sulfur dioxide and carbon dioxide have unusual solubilities in btoh ethylcellulose and nitrocellulose, which indicate chemical effects.   Chemical effects for the acid-base interaction of carbon dioxide in benzene have been reported.[6]

The volume of helium adsorbed in both ethylcellulose and nitrocellulose was also unusually high.   This may be due to the "hole filling" of the micropores in the films by this small molecule.   It has been reported that the rather stiff, thick chains of ethylcellulose in a random network can leave gaps large enough for occupancy by penetrant molecules.[16]

The solubility data presented in Tables I and II do not show a linear relationship of the log of volumetric concentrations of the gases with the Lennard-Jones force constants.[12]   However, they show a linear increase

TABLE III

Lennard-Jones Force Constants and Solubility Constants of Gases

Gas	Lennard-Jones force constant ϵ/k, °K.	Solubility at 25°C. in ethylcellulose S, g./cc. cm. Hg × 10⁵		Solubility at 25°C. in nitrocellulose S, g./cc. cm. Hg × 10⁵	
		Volumetric[a]	Gravimetric[b]	Volumetric[a]	Gravimetric[b]
He	10[c]	—	0.0432	—	0.029
N_2	95[c]	0.261	0.234	0.109	0.073
O_2	118[c]	0.345	0.330	0.271	0.188
A	120[c]	0.472	0.453	0.286	0.261
CO_2	189[c]	4.05	3.93	2.58	1.90
SO_2	331[d]	142.2	102.7	63.3	27.9
NH_3	312[d] 320[e]	45.9	36.7	93.8	55.1
H_2O	498[d] 380[e]	—	2510.0	—	1932.0
C_2H_6	243[c]	10.0	6.48	7.14	6.47
C_3H_8	284[d]	30.1	24.80	10.5	7.74
$n-C_4H_{10}$	328[d]	100.6	68.8	6.44	3.82
$n-C_5H_{12}$	362[d]	303.0	85.9	—	—
$n-C_6H_{14}$	391[d]	937.0	237.0	—	—

[a] From volumetric absorption method.
[b] From gravimetric absorption method.
[c] Calculated from second virial coefficient.[20a]
[d] Calculated from $Tc/1.3$[20b]
[e] Corrected for electrostatic interaction of the two dipoles.[20c]

with Lennard-Jones force constants when they are expressed on a weight basis (Table III), as illustrated in Figures 2 and 3 for ethylcellulose and nitrocellulose films, respectively.

In principle, for polar molecules, such as water and ammonia, the Stockmayer potential[17] must be used instead of the Lennard-Jones force constant. However, the Lennard-Jones force constants fit the curve better than the Stockmayer potentials. The Stockmayer potential consists of the Lennard-Jones function and an angle-dependent term that is used to account for the electrostatic interaction of the two dipoles.

Diffusion Coefficients

Diffusion coefficients for ethylcellulose and nitrocellulose computed from the equation, $P = 10DS$, are listed in Tables I and II, and are plotted against the molecular weights of the penetrants on a log–log scale, as shown in Figures 4 and 5, respectively. A conversion factor of 10 was incorporated in this equation for dimensional purposes to facilitate calculations. The
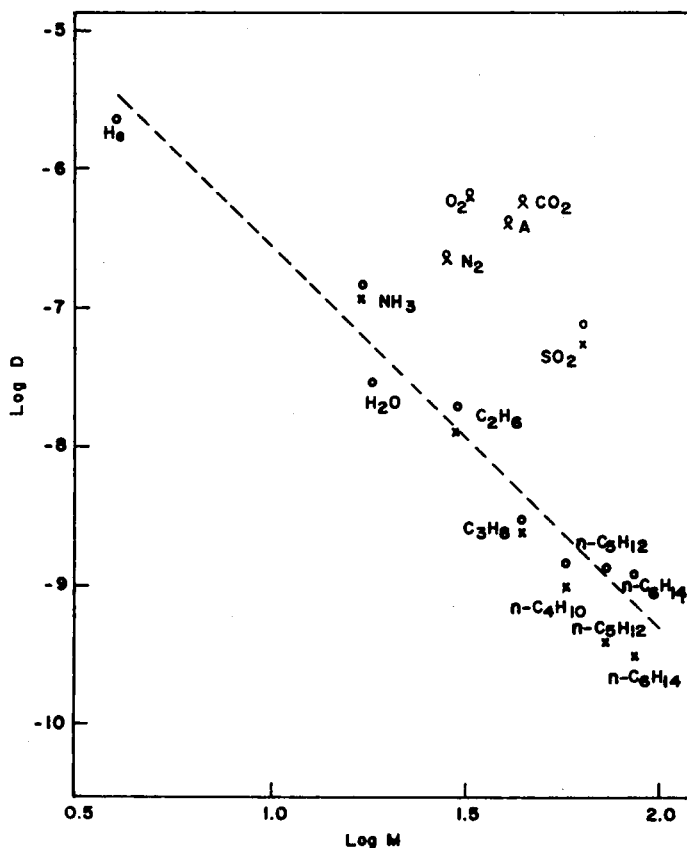

Fig. 4. Diffusion coefficients of molecules in ethylcellulose vs. molecular weights: (O) gravimetric adsorption; (×) volumetric adsorption.
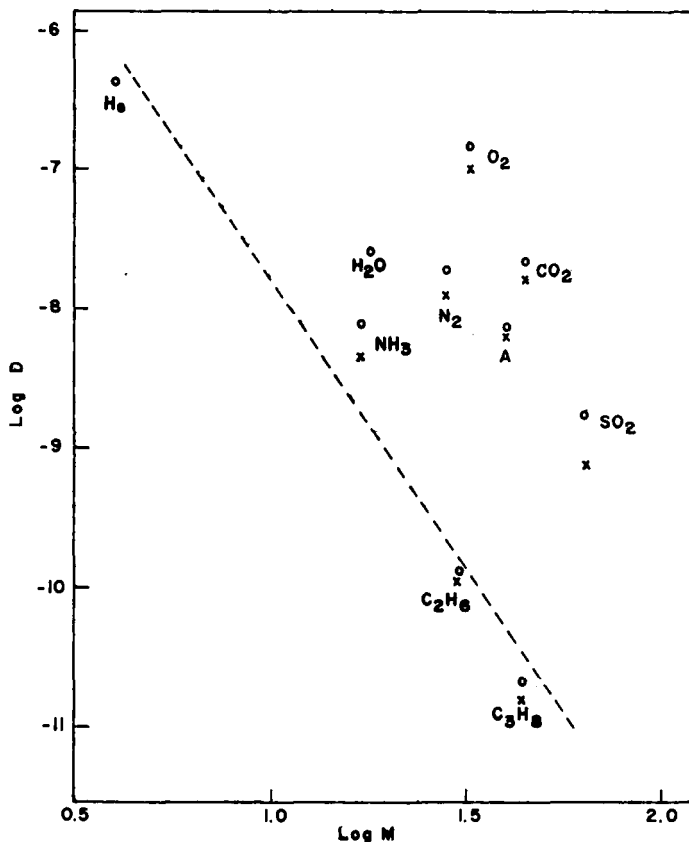
Fig. 5. Diffusion coefficients of molecules in nitrocellulose vs. molecular weights: (O) gravimetric adsorption, (×) volumetric adsorption.

values of S are expressed in cubic centimeters of gas per cubic centimeter of adsorbent.

Figures 4 and 5 show that the diffusion coefficients for the gases studied here did not fall on the same straight line but did tend to show a decrease in value with an increase in molecular weight. Two things can contribute to such displacement of the curves in both Figures 4 and 5: (*1*) The shape factor of the molecules, which was over-simplified in the derivation of equations. (*2*) The application of the equation, $P = DS$.

Since the equation was derived on the assumption that Henry's law applies for solubility and since the adsorption isotherms indicated that Henry's law is not obeyed in some cases, the diffusion coefficients calculated from this equation are not theoretically justified. According to the equation, it appears that both diffusion and solubilization contribute independently to the permeability. This effect is true when solubilization of the penetrant does not change the physical structure of the film. In cases where the penetrant swells the film or is tightly bound into its macro-

molecular structure, the phenomenon of the permeation process is further complicated. The diffusion will not be independent of the concentration of adsorbed molecules, in this case.

It is noted that there is quite a difference in diffusion between nitrogen and oxygen, although they have very similar physical properties. The same difference in behavior between nitrogen and oxygen can be found in recent reports from the permeability measurements for the various polymer films with nitrogen and oxygen.[4, 15, 18, 19]

The solubilization, diffusion, and permeation of the molecules determined are higher in ethylcellulose than in nitrocellulose. This is considered to be not because of the differences in crystallinity but because of the differences in compactness of the molecular arrangement in the films. (The x-ray diffraction patterns indicated that both films are noncrystalline. The density of nitrocellulose film is 1.46 while that of ethylcellulose is 1.10.)

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Synopsis

Permeability of ethylcellulose and nitrocellulose films to thirteen different gases and vapors was determined. The solubility of these gases and vapors in ethylcellulose and

nitrocellulose was also measured by gravimetric and volumetric methods of equilibrium sorption. From these data for permeability and solubility, diffusion coefficients of the gases and vapors in the polymeric films were calculated by means of the relation, $P = DS$, in which P and S are the permeability and solubility constants, respectively. It was found that the diffusion coefficient D decreased linearly with an increase of molecular weight; however, the shape factor of the molecules played an important role in the diffusion process. The solubility constants increased linearly with an increase of the Lennard-Jones force constants ϵ/k when solubility was expressed on a weight basis rather than a volume basis. Both ethylcellulose and nitrocellulose are noncrystalline. Higher solubility, diffusibility, and permeability of ethylcellulose than that of nitrocellulose are considered to be due to the molecular packing in the films.

Résumé

On a déterminé la perméabilité de films d'éthyl-cellulose et de nitrocellulose vis-à-vis de treize gaz et vapeurs différents. On a aussi mesuré la solubilité de ces gaz et vapeurs dans l'éthylcellulose et la nitrocellulose par des méthodes gravimétriques et volumétriques de sorption d'équilibre. A partir de ces données pour la perméabilité et la solubilité on a calculé les coefficients de diffusion de gaz et des vapeurs dans les films de polymères au moyen de la relation $P = DS$, dans laquelle P et S sont respectivement les constantes de perméabilité et de solubilité. On a trouvé que le coefficient de diffusion D décroît linéairement avec une augmentation du poids moléculaire; cependant la forme des molécules joue un rôle important dans le processus de diffusion. Les constantes de solubilité croissent linéairement avec une croissance des constantes ϵ/k de la force de Lennard-Jones, lorsque la solubilité s'exprimait sur la base du poids plutôt que sur base du volume. L'éthylcellulose et la nitrocellulose sont toutes deux non-cristallines. On considère que la plus grande solubilité, diffusibilité et perméabilité de l'éthylcellulose par rapport à la nitrocellulose sont dues au tassement moléculaire dans les films.

Zusammenfassung

Die Permeabilität von Äthylcellulose- und Nitrocellulosefolien für dreizehn verschiedene Gase und Dämpfe wurde bestimmt. Auch die Löslichkeit dieser Gase und Dämpfe in Äthylcellulose und Nitrocellulose wurde durch gravimetrische und volumetrische Bestimmung der Gleichgewichtssorption bestimmt. Aus den Permeabilitäts- und Löslichkeitsdaten wurden mit Hilfe der Beziehung $P = DS$, wo P und S die Permeabilitäts—bzw. Löslichkeitskonstanten sind, die Diffusionskoeffizienten der Gase und Dämpfe in den Polymerfolien berechnet. Der Diffusionskoeffizient D nimmt mit zunehmendem Molekulargewicht linear ab; es spielt aber der Gestaltsfaktor der Moleküle eine wichtige Rolle für den Diffusionsprozess. Bei Darstellung der Löslichkeit auf Gewichtsbasis anstatt auf Volumsbasis nahm die Löslichkeitskonstante linear mit einer Zunahme der Lennard-Jones-Kraftkonstanten, ϵ/k, zu. Sowohl Äthylcellulose als auch Nitrocellulose sind nicht kristallin. Die höhere Löslichkeit, Diffusionsfähigkeit und Permeabilität in Äthylcellulose in Vergleich zu Nitrocellulose werden auf die Molekülpackung in den Folien zurückgeführt.