

Diffusion and Solubility of *n*-Alkanes in Polyolefines

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Synopsis

The diffusion and partition coefficients (relative solubility constants) of *n*-alkanes (from carbon nos. 12–32) have been determined by a permeation method (pouch method) for the polyolefines LDPE, HDPE, and PP-copolymer, and PP-homopolymer at room temperature. The activation energies for the diffusion are interpreted in the meaning of the rate transition theory. Correlations exist between the activation energy ΔE and the heat of vapourization $\Delta_v H_v$, as well as between the activation energy ΔE and the Arrhenius preexponential factors D_0 . These correlations are useful for the prediction of the diffusion coefficients of *n*-alkanes with carbon numbers larger than 32.

INTRODUCTION

The diffusion of gases and organic vapours through different polymers has been the topic of many publications, especially in view of the fitness of some diffusion theories which try to explain the temperature and concentration dependance of the diffusion phenomenon.¹

We have been interested in the permeation of volatile aroma components through polymers for a long time on account of packaging technical reasons because the quality of food and cosmetics rich in aroma components depends to a great deal on the transmission behavior of the packaging material in relation to the aroma components.

Our interest is focused not only on volatile but also on less or sparingly volatile organic compounds because diffusion and solubility are the main factors determining the permeation as well as the migration rate. The problems of the contamination of the food arising from migration of components of the packaging material are well known. Less known is the potential contamination by permeation of less volatile organic compounds. Because the last process could be of the same importance for the quality decrease as the first one, it seemed worthwhile investigating the permeation of less volatile organic compounds.

As model compounds for studying the diffusion of sparingly volatile compounds we have selected the *n*-alkanes from carbon nos. 12–32. Because of the chemical inertness the analytical handling of this class of compounds is very easy. The results obtained from these compounds should be very interesting and transferable to a variety of other substances which are derivatives of the *n*-alkanes.

MATHEMATICAL RELATIONS

The permeation of a substance out of a finite reservoir through a polymer membrane into a finite volume represents a diffusion problem with finite boundary conditions which can easily be treated by Laplace transformation.

The diffusion of a substance out of a volume v_i through a membrane of the thickness l into the outer volume v_a is described by the following well-known differential equation, with D the diffusion coefficient, which is assumed to be independent of concentration, and C the concentration

$$D \cdot \frac{d^2 C}{dx^2} = \frac{dC}{dt} \quad (1)$$

with the following boundary conditions for $C(x,t)$,² where S is a partition coefficient and A is the membrane area:

$$C(0,0) = 0 \quad (2)$$

$$C(l,0) = 0 \quad (3)$$

$$C(0,t) = C = S \cdot c_i \quad (4)$$

$$C(l,t) = C = S \cdot c_a \quad (5)$$

$$c_i = c_0 = \frac{D \cdot A}{v_i} \int_0^t \left(\frac{dc}{dx} \right)_{x=l} dt \quad (6)$$

$$c_a = \frac{D \cdot A}{v_a} \int_0^t \left(\frac{dc}{dx} \right)_{x=0} dt \quad (7)$$

Applying the Laplace operator $L = \int_0^\infty \exp(-pt)$ to the equations above, we get the following new equation set with Laplace transformed magnitudes which are indicated by crosslines:

$$D \frac{d^2 \bar{c}}{dx^2} = p \bar{c} - C(x,0) \quad (1')$$

$$\bar{c}(0,p) = \bar{c} = S \cdot \bar{c}_i \quad (4')$$

$$\bar{c}(l,p) = \bar{c} = S \cdot \bar{c}_a \quad (5')$$

$$\bar{c}_i = \bar{c}_0 - \frac{D \cdot A}{p \cdot v_i} \left(\frac{d\bar{c}}{dx} \right)_{x=l} \quad (6')$$

$$\bar{c}_a = \frac{D \cdot A}{p \cdot V_a} \left(\frac{d\bar{c}}{dx} \right)_{x=0} \quad (7')$$

The solution of the transformed equations gives for the concentration \bar{c}_a

in the outer volume:

$$\bar{c}_a = \frac{a_2 \cdot c_0}{(a_1 a_2 / q^2 - 1) \cdot q \cdot \sin q + (a_1 + a_2) \cos q} \tag{8'}$$

with

$$a_1 = (S \cdot A \cdot l) / v_i, a_2 = (S \cdot A \cdot l) / v_a, \text{ and } iq = l \cdot (p/D)^{1/2}.$$

Transforming the solution of \bar{c}_a back to c_a , we get

$$\begin{aligned} c_a = & \frac{a_2 c_0}{a_1 a_2 + a_1 + a_2} \\ & - a_2 c_0 \sum_{n=1}^{\infty} \left(\exp \left[-\frac{(q_n^2 \cdot D \cdot t)}{l^2} \right] \right) \\ & \times \left\{ \frac{q_n}{2} \left[\left(a_1 + a_2 + \frac{a_1 \cdot a_2}{q_n^2} + 1 \right) \cdot \sin q_n + \left(1 - \frac{a_1 a_2}{q_n^2} \right) q_n \cdot \cos q_n \right] \right\}^{-1} \end{aligned} \tag{8}$$

where

$$\tan q_n = \frac{(a_1 + a_2) q_n}{q_n^2 - a_1 a_2} \tag{9}$$

For long times the series converges very rapidly so that all the q_n 's greater than q_1 are negligible, then we get

$$\ln \left(\frac{a_2 c_0}{a_1 a_2 + a_1 + a_2} - c_a \right) = \ln[A] - \frac{q_1^2 \cdot D \cdot t}{l^2} \tag{10}$$

where

$$\begin{aligned} [A] = a_2 c_0 \left\{ \frac{q_1}{2} \left[\left(a_1 + a_2 + \frac{a_1 \cdot a_2}{q_1^2} + 1 \right) \cdot \sin q_1 \right. \right. \\ \left. \left. + \left(1 - \frac{a_1 \cdot a_2}{q_1^2} \right) \cdot q_1 \cdot \cos q_1 \right] \right\}^{-1} \end{aligned}$$

that means from the slope of the straight line of the curve of eq. (10) we can calculate the diffusion coefficient. At our experimental conditions $a_1 + a_2 + a_1 a_2$ has always been lower than 0.1 so that $\tan q_1 = (a_1 + a_2) q_1 / (q_1^2 - a_1 a_2)$ can be replaced by $q_1 = \sqrt{a_1 + a_2 + a_1 a_2}$ with less than 5% error.

Equation (8) represents the exact unsteady state condition. But under practical conditions the system can reach up very close to the pseudo-steady-

state condition as we could observe at our experiments. For this case one can apply the following equation³:

$$\ln \frac{c_0 v_i / (v_i + v_a + S \cdot A \cdot l)}{c_0 v_i / (v_i + v_a + S \cdot A \cdot l) - c_a} = \frac{P \cdot A \cdot (v_i + v_a + S \cdot A \cdot l)}{l \cdot v_i [v_a + (S \cdot A \cdot l) / 2]} \cdot t \quad (11)$$

Analyzing either with exact equation or the equation for the quasi-steady-state condition, the solubility constant S has to be known, if the diffusion coefficient has to be calculated. Measuring P , one can always choose the parameters v_a so that $S \cdot A \cdot l / 2 \ll v_a$, which means that all the terms with the solubility constant S in eq. (11) can be neglected.

EXPERIMENTAL

The permeation study has been carried out with the so-called pouch method described in detail elsewhere.³ Applying this method, a solution containing the permeate is transferred to a polymer pouch, which has been formed from a polymer film by welding three of its sides. After loading the pouch with a solution of the permeate, the pouch has been heat-sealed and dipped into a bath of 500–1000 mL of pure solvent, which has been located in a 1-L wide-necked bottle. If required, the solution in the bottle can be stirred with a magnetic stirrer and a rod magnet.

By analyzing 0.5–1.0 mL amounts of the outer solution at given times by gas chromatography, the time-dependent increase of the permeate concentration in the outer solution has been determined. Then, the permeation or diffusion constants have been calculated either by eq. (10) or (11).

The advantage of this method is based on three main factors: First, the high sensitiveness of the analytical method. Second, the permeation measurement of substances in highly diluted solutions which avoids the swelling of the polymer if wanted by choosing the right solvent. Also, this permits the measurement of more than one permeate simultaneously because in the highly diluted state the interference of the diffusing molecules can be neglected. Last but not least, the analogy between the polymer pouch and a real polymer package which allows one to study the quality decrease of packed products by loss of permeable components under real practical conditions.

The following polymers have been used:

Low density polyethylene (LDPE)	Hostalen	LDH 1018,	$\rho = 0.918 \text{ g/cm}^3$
High density polyethylene (HDPE)	Hostalen	GF 4760,	$\rho = 0.956 \text{ g/cm}^3$
Polypropylene-copolymer (PP-cop.)	Hostalen	PPH 1022,	$\rho = 0.900 \text{ g/cm}^3$
Polypropylene-homopolymer (PP-homop.)	Hostalen	PPH 1050,	$\rho = 0.902 \text{ g/cm}^3$

The mean thickness of the polymers (50 or 100 μm) has been determined with a measuring apparatus manufactured by Mahr (Dickenmessgerät, Esslingen, West Germany).

The n -alkanes were purchased from Fluka (highest available quality) and used without further purification.

QUESTIONS CONCERNING THE DIMENSIONS OF THE SOLUBILITY AND PERMEATION CONSTANT

The dimension of the permeation constant which is the product of the diffusion and solubility constant will be determined by the dimension of the solubility constant. Barrer,⁴ who first introduced the permeation constant, defined the solubility constant as the ratio of the concentration of a substance in a solid phase (polymer) to the vapor pressure of the same substance staying in contact with the solid phase. This definition demands the determination of the vapor pressure of the permeate. This is not so difficult when having a pure substance and if the vapor pressure of the substance itself is great enough. But, dealing with a solution, the partial pressure has to be measured. Determining the partial pressure, we can apply Raoult's law in its generalized form which states that the partial pressure p over a solution is proportional to the vapor pressure p^0 of the pure substance, the mol fraction x and the activity coefficient γ :

$$p = p^0 \cdot x \cdot \gamma \quad (12)$$

Measuring the partial vapor pressure is not easy. It is well known that its determination, even with headspace chromatography, leads to very bad results because of adsorption phenomena at the syringe and column system.⁵

For highly diluted systems, we get for the mol fraction x of the component i :

$$x_i = \frac{n_i}{\sum_i n_i} \cong \frac{n_i}{n_s} = \frac{c_i M_s}{\rho_s} \quad (13)$$

where n , c , M , and ρ are the moles, the concentration, the molecular weight, and the density and the index i and s refer to the component i and the solvent s , respectively.

Now, assuming that γ can be regarded as a coefficient at infinite dilution, we get for the partial vapor pressure p

$$p = p^0 c_i \frac{M_s}{\rho_s} \gamma \quad (14)$$

The last relation states that the partial pressure over a highly diluted solution is proportional to the concentration in solution. Therefore, we are able to define a solubility constant where the concentration of the permeate in the solid phase c_p refers to its concentration in solution c_i :

$$S_r = c_p / c_i \quad (15)$$

This constant is denoted as the relative solubility constant (therefore the index r) in contrast to S , the absolute solubility constant, and—because it

is a dimensionless quantity—it is nothing else but a partition coefficient. This constant is a practical one and easily measured, though it is dependent on the nature of the solvent and concentration dependent for less diluted systems. If p_0 and γ are known, S_r is easily transformed to S .

RESULTS

Diffusion

Table I shows the diffusion coefficients of some *n*-alkanes (from carbon nos. 12–32) in some polyolefines. These constants have been calculated from experimentally determined relative permeation and solubility constants by permeation experiments of diluted alkane solutions (Table II).

Figure 1 shows these constants as functions of the diffusion constants of the *n*-alkanes in LDPE where the alkanes have been dissolved in hexane. The straight line with the slope one in the log/log plot represents the diffusion constants in LDPE with hexane as solvent. All the other curves show the relative and absolute graduation to this system.

The application of a completely apolar solvent (hexane) and of an extremely polar solvent (methanol) shows the ability of the polymer to swell which is reflected by the alteration of the diffusion coefficients.

The shapes of the different curves show similiar diffusion behavior in LDPE and HDPE. The graduation of the diffusion coefficients for the four solvents is the same in LDPE and HDPE whereas the absolute values of the diffusion coefficients in HDPE are eight to ten times lower than in LDPE. This may essentially be caused by the different grade of crystallinity of the two polymers as the different densities ρ (LDPE) = 0.918 g/cm³ and ρ (HDPE) = 0.956 g/cm³ imply; but we have not investigated the influence of the crystallinity on the diffusion in detail, because we are not so interested in the influence of the polymer on the diffusion but more in the influence of the properties of the diffusing molecule on the diffusion. The slopes of the LDPE and HDPE curves are almost identical. In comparison to this, the PP curves are a little flatter but also show a constant graduation for the four solvents. Therefore, the diffusion coefficients for the higher alkanes which could not be measured in the polar solvents because they were not soluble enough could be fairly estimated from the data obtained in hexane.

The alteration of the diffusion coefficients for LDPE and HDPE is marked by the factor 40 but for PP by the factor 7300 if replacing the solvent methanol by hexane. Also acetone is able to swell PP much more than LDPE and HDPE.

A very interesting question is whether the trend of the individual alkane diffusion coefficients are correlative with alkane specific properties. All known theories of the diffusion behavior of low molecular compounds in polymers fall back upon two theories which were developed for liquids: the model of Sutherland and Einstein and that of Eyring.

Following Einstein,⁶ we get for the diffusion constant D

$$D = \frac{K \cdot T}{6\pi\eta r} \quad (16)$$

TABLE I
 Diffusion coefficients of n-alkanes with n carbon atoms at 23° C for LDPE, HDPE, PP-copolymer und PP-homopolymer, alkanes dissolved in methanol, ethanol, acetone and hexane

Solvent polymer	$D \times 10^{10} \text{ (cm}^2\text{/s)}$											
	12	14	16	18	20	22	24	26	28	30	32	
Methanol												
LDPE	27	25	15	12	4.7							
HDPE	6.4	4.9	2.9	1.9	0.9							
PP-cop.	1.1	0.82	0.74	0.66	0.61							
PP-homop.	0.59	0.43	0.37	0.34	0.31							
Ethanol												
LDPE	34	18	14	10	8.3	4.6						
HDPE	5.6	3.1	2.1	1.4	0.80	0.33						
PP-cop.	0.52	0.39	0.28	0.30	0.30	0.29						
PP-homop.	0.46	0.34	0.29	0.26	0.27	0.26						
Acetone												
LDPE	97	65	54	37	22	13						
HDPE	19	13	9.1	6.2	3.3	1.3						
PP-cop.	14	11	9.1	8.0	7.8	6.5						
PP-homop.	12.5	10	8.6	7.5	7.3	6.6						
Hexane												
LDPE	1300	1000	820	600	400	240	150	81	54	29	11	
HDPE	380	320	190	116	50	20	15.	8.5	4.6	2.6	1.2	
PP-cop.	2400	2200	2200	2300	2000	1500	1400	1300	1000	770	430	
PP-homop.	3400	2800	2500	2100	1700	1300	1000	720	690	540	390	

TABLE II
Relative Solubility Constants S_r and Permeation Constants $P_r \times 10^{10}$ (cm²/s) of Alkanes with n Carbon Atoms at 23°C
for LDPE, HDPE, PP-Copolymer and PP-Homopolymer^a

Solvent polymer	12		14		16		18		20		22		24		26		28		30		32	
	S	P	S	P	S	P	S	P	S	P	S	P	S	P	S	P	S	P	S	P	S	P
Methanol																						
LDPE	2.8	76	3.8	97	5.9	89	11	132	23	110												
HDPE	2.5	16	3.5	17	5.8	17	11	21	27	24												
PP-cop.	4.4	4.4	5.6	4.6	7.3	5.4	10	6.6	14	8.5												
PP-homop.	3.5	2.1	4.7	2.0	5.9	2.2	8.0	2.7	11	3.4												
Ethanol																						
LDPE	0.97	33	1.3	23	1.6	22	2.5	26	4.2	35	8.1	37										
HDPE	0.94	5.3	1.3	4.0	1.6	3.4	2.6	4.3	5.9	4.7	13	4.3										
PP-cop.	1.5	0.78	1.7	0.87	1.7	0.47	1.9	0.57	2.2	0.67	2.7	0.78										
PP-homop.	1.3	0.61	1.5	0.51	1.5	0.43	1.7	0.44	1.9	0.51	2.3	0.61										
Acetone																						
LDPE	0.58	56	0.69	45	1.0	54	1.8	66	3.2	70	6.2	79										
HDPE	0.52	10	0.67	9.0	1.1	10	2.1	13	4.3	14	9.4	12										
PP-cop.	0.79	11	0.87	9.4	1.1	10	1.5	12	1.8	14	2.3	15										
PP-homop.	0.72	9.0	0.77	7.8	0.97	8.3	1.3	9.7	1.5	11	1.8	12										
Hexane																						
LDPE	0.24	310	0.22	220	0.24	197	0.30	180	0.32	130	0.41	98	0.39	59	0.48	39	0.66	36	0.97	28	1.3	14
HDPE	0.15	57	0.15	48	0.19	36	0.29	34	0.42	21	0.70	14	0.84	8.1	0.63	5.4	0.99	4.6	1.4	3.6	2.1	2.5
PP-cop.	0.30	720	0.28	620	0.29	640	0.30	690	0.30	600	0.32	480	0.28	390	0.28	360	0.28	280	0.29	220	0.36	155
PP-homop.	0.21	710	0.19	530	0.18	450	0.18	380	0.17	290	0.18	230	0.16	160	0.16	115	0.14	97	0.13	70	0.15	59

^a Alkanes dissolved in methanol, ethanol, acetone, and hexane.

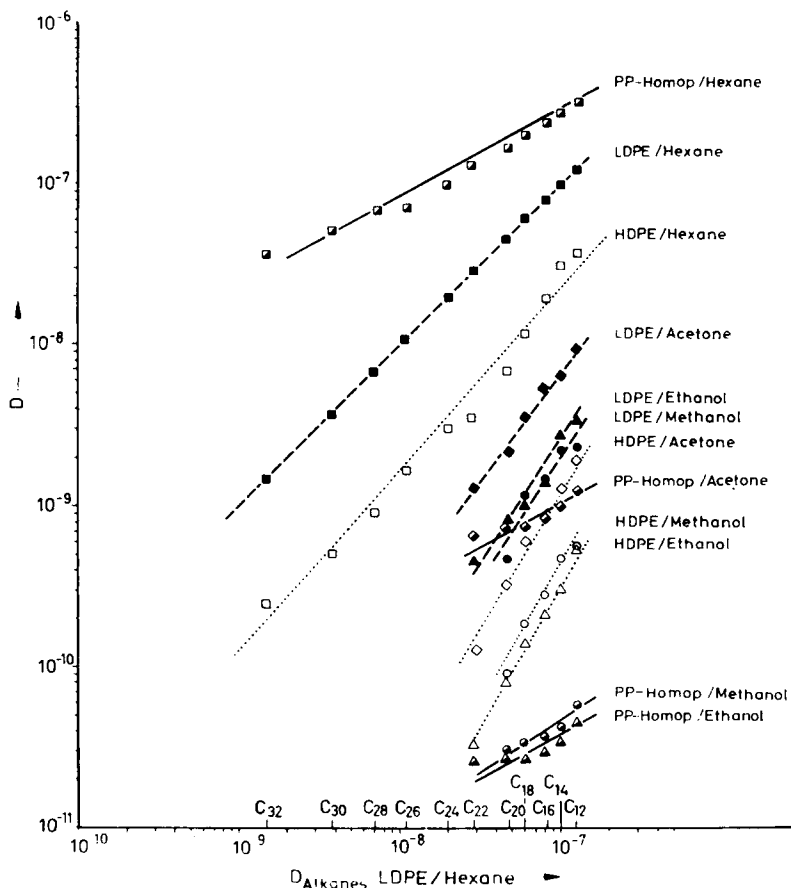


Fig. 1. Correlation of the diffusion coefficients of *n*-alkanes in LDPE, HDPE, and PP-homopolymer as function of the diffusion coefficients of the alkanes in swollen LDPE (hexane as solvent), alkanes dissolved in methanol, ethanol, acetone, and hexane.

with K the Boltzmann constant, T the absolute temperature, η the viscosity of the solvent, and r the radius of the diffusing molecule.

By holding T and η constant, D is inversely proportional to r or the cube root of V , the molar volume of the substance. This model is exactly valid only for ideal liquids whereby the diffusing molecule has to be larger than the molecule of the liquid. Sutherland⁷ introduced a correction factor expanding the applicability of the equation above to cases where diffusing and liquid molecule are of the same size. But in both cases a spherical shape of the molecule is required.

Although it is clear that the polyolefines are no liquids and that they can only reservedly regarded as highly viscous liquids, it may be worthwhile comparing the diffusion in a liquid system with the diffusion in a polymeric system in view of the Stokes-Einstein model. In the following we show two diagrams where we see a correlation of the diffusion constants vs. $V^{-1/3}$ assuming that the alkanes have spherical conformation in solution. The molar volumes have been calculated by increments given by Kopp⁸ (with a value of 11 cm³ for carbon and 5.5 cm³ for hydrogen). Figure 3 shows a correlation of the diffusion constants of some *n*-alkanes in tetrachlorome-

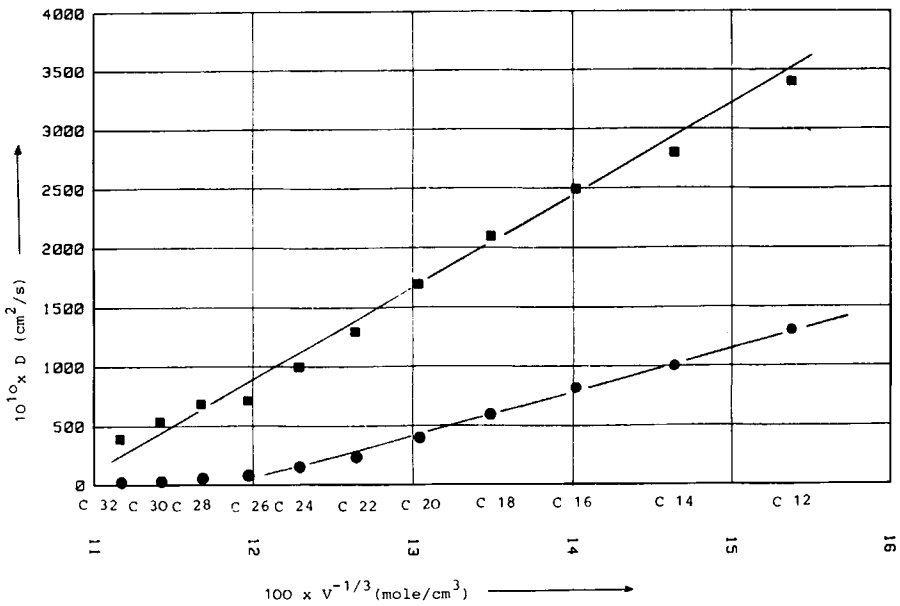


Fig. 2. Correlation of the diffusion coefficients of the *n*-alkanes in LDPE (●) and PP-homopolymer (■) with the cube roots of Kopp's molevolumes, alkanes solved in hexane.

thane. The diffusion constants of the *n*-alkanes in solution follow the Stokes-Einstein relation very well whereas in the case of the polyolefines (Fig. 2) only PP shows a good correlation. From this we can conclude that the structure of PP swollen with hexane shows the greatest resemblance to a liquid.

Meerwall and Ferguson,¹⁰ who have measured the diffusion constants of

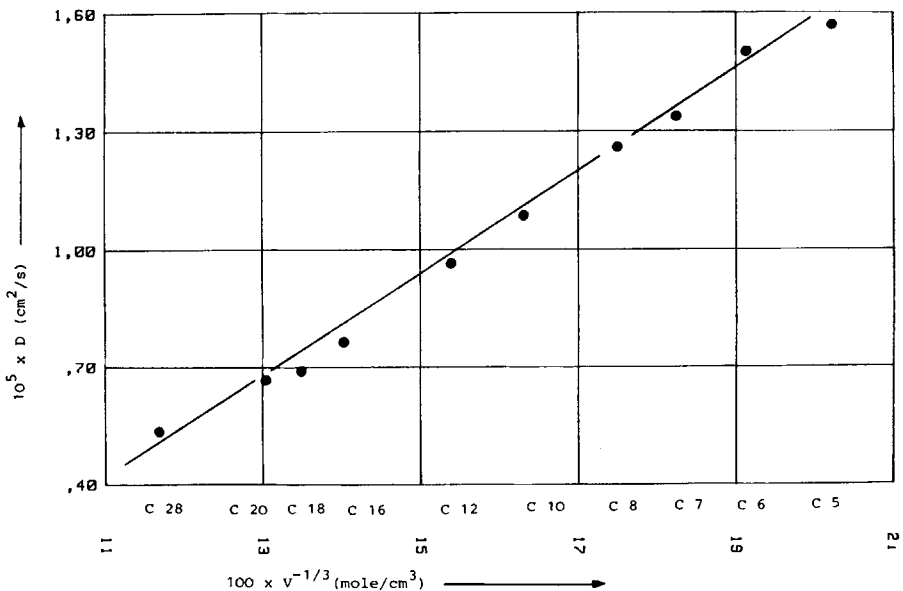


Fig. 3. Correlation of the diffusion coefficients of the alkanes in tetrachloromethane with the cube roots of Kopp's molevolumes, data taken from Dewan and van Holde.⁹

ten *n*-alkanes (octane to hexatriacotane) in uncrosslinked rubber by spin echo experiments, find a linear correlation between the reciprocal diffusion coefficients and the molecular weight of the diffusing species. Such a correlation does not exist for the diffusion of *n*-alkanes in polyolefines. Eyring et al.^{11,12} apply the rate transition theory to the diffusion process. They find for the diffusion coefficient in liquid phase

$$D = \frac{K \cdot T}{h} \cdot \lambda^2 \cdot \frac{f}{f^\#} \exp(-\epsilon_0/RT) \quad (17)$$

with *K* the Boltzmann constant, *h* the Planck constant, *T* the absolute temperature, λ the jump distance of a molecule after the activation step, *f* and *f*[#] the partition functions in the ground and activated state, ϵ_0 the activation energy at 0 K, and *R* the universal gas constant. Supposing the partition functions of the rotation and vibration are unchangeable in the ground and activated state the equation above becomes

$$D = \frac{\lambda^2}{v_f^{1/3}} \left(\frac{K \cdot T}{2\pi m} \right)^{1/2} \exp(-\epsilon_0/RT) \quad (18)$$

with *v_f* the free volume and *m* the mass. This equation which has been derived for the self-diffusion coefficient of liquids has been applied to the case of interdiffusion by Eyring and co-workers, too. They assumed that in the case of interdiffusion ϵ_0 , λ , and *v_f* becomes $x_1\epsilon_{01} + x_2\epsilon_{02}$, $x_1\lambda_1 + x_2\lambda_2$, and $x_1v_{f1} + x_2v_{f2}$, and the mass *m* becomes the reduced mass μ . Having a very diluted system, the sum of ϵ_0 , λ , and *v_f* becomes $\epsilon_{0\text{ solv}}$, $\lambda_{\text{ solv}}$, and *v_{f solv}*. Then, if comparing the diffusion of a homologous series, the alteration of the diffusion coefficients will be determined by the different masses. But, operating with the reduced mass, one implies that the two masses are involved in the activation step and then the activation energy must become the mean of its sum, namely $(\epsilon_{01} + \epsilon_{02})/2$. Now, if comparing a homologous series again, the different diffusion coefficients are determined by the different activation energy of each homologue. Therefore, because the situation is not quite clear, we have to prove if *D* correlates better with $1/\sqrt{\mu}$ or $\ln D$ better with ϵ_0 (or exactly $\ln(D \cdot \sqrt{\mu})$ with ϵ_0). The influence of the preexponential factor is normally not as large as that of the exponential factor so that we may expect a correlation of $\ln D$ with ϵ_0 . Here again we have to point out that these considerations are only justified if we regard two miscible liquids. In the case of a liquid solved in a polymer the application of this theory is not quite correct, of course. Nevertheless, we do this to see the difference of the diffusion in a liquid to a polymer system in the meaning of the rate transition theory. Eyring et al. had found that the activation energy of the straight chain alkanes is a quarter of their heats of vaporization, ΔH_v . Hence, we can replace ϵ_0 by ΔH_v . As heats of vaporization we have chosen those at the boiling temperature ($\Delta_v H/s$), which we have calculated by Trouton's rule ($\Delta_v H_s/T_s \cong 21.5$ cal/mol).

The upper curve of Figure 4 shows the diffusion coefficients of alkanes in tetrachloromethane as a plot of $\ln D$ with $\Delta_v H_s$. The correlation is

excellent. We observe a strong proportionality between the logarithms of the diffusion coefficients and the heats of vaporization, showing that the considerations above are not quite useless. A correlation of $\ln(D\sqrt{\mu})$ vs. $\Delta_v H_s$ or D vs. $1/\sqrt{\mu}$ also gives straight lines, but with the exception of pentane in each curve, which shows a significant deviation. Therefore, these two plots are not shown here.

The three lower curves in Figure 4 show the diffusion coefficients in PP, LDPE, and HDPE where hexane served as solvent for the alkanes as plots of $\ln D$ vs. $\Delta_v H_s$. Only in this solvent the determination of the diffusion coefficients of the alkanes up to carbon no. 32 has been possible. The comparison of the different correlations of the diffusion coefficients in the polymers with the correlation of the diffusion coefficients in tetrachloromethane shows that PP behaves like a liquid analogous to the Stokes-Einstein model whereas LDPE, and more so, HDPE, differ from this behavior. The deviation increases with growing carbon number. The reason for this deviation from linearity may be caused by the largeness of the "holes" in the polymer, which the alkanes have to their disposal on the way through the polymer. In the case of PP the polymer matrix still seems to accommodate to the size of the diffusing molecules whereas in the case of LDPE and HDPE it looks as if the "holes" in the polymer are too small for alkanes bigger than C 16 and C 18 so that the alkanes could not migrate in an elemental step. The now additionally required energy would explain the deviation of the diffusion coefficients in the direction of too small values.

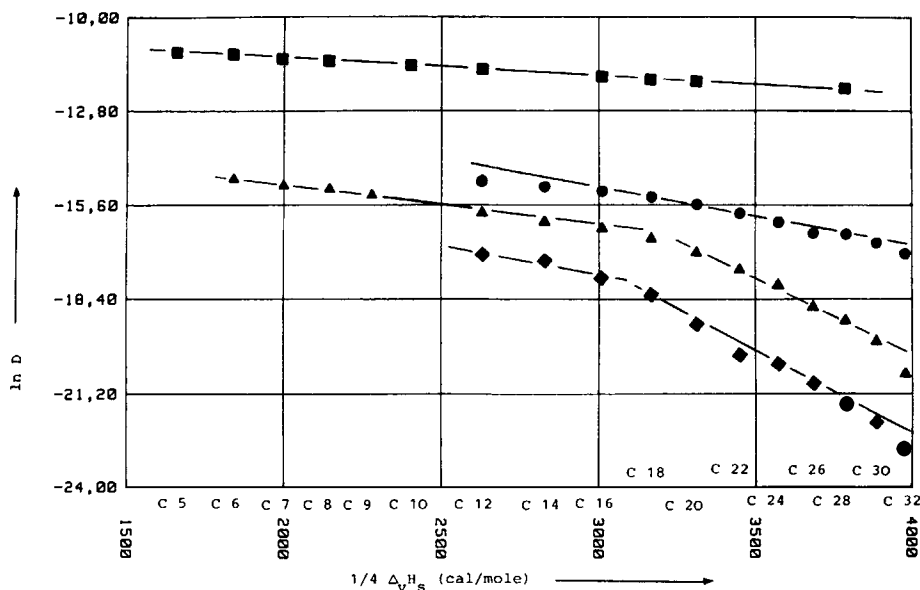


Fig. 4. Correlation of the diffusion coefficients of *n*-alkanes in tetrachloromethane (■) and by (hexane) swollen polyolefines LDPE (▲), HDPE (◆), and PP (●) with the molar heats of vaporization of the alkanes; data of hexane, heptane, octane and nonane are taken from Ref. 18.

Temperature Dependence of the Diffusion Coefficient

The temperature dependence on diffusion of the alkanes in the polyolefines has been examined only for LDPE (Table III). The temperature dependence of the diffusion coefficients of the alkanes in LDPE is of an Arrhenius type in the investigated region of + 6°C to + 40°C, as has been observed by other authors, too¹³ (Table IV). The interpretation of the activation energies within the meaning of the Eyring model may let us expect a linear correlation of the activation energy ΔE or the activation enthalpy ΔH^\ddagger with the heats of vaporization at the boiling point $\Delta_v H_s$. The corresponding relation of the activation energies of the self-diffusion of the alkanes with the heats of vaporization corroborates this linear relation (Fig. 5).

The activation energies of the diffusion of the alkanes in LDPE, where ethanol or hexane served as solvent, correlated with the heats of vaporization show linear curves with an inflection point (Fig. 6). The inflection points indicate that we might have a change in the mechanism at the elemental activation step. An explanation of this behavior may be given again by the holes of the polymer which are built by the fluctuation of the segments of the polymer chains. The curves with the flatter slopes may represent liquidlike behavior where a certain part of the heat of vaporization serves as activation energy and where the holes in the polymer are larger than the diffusing molecules. The curves with the steeper slopes may indicate that now the holes are smaller than the diffusing molecules. Now the molecule has to bring up additional energy to overcome the van der Waals forces of the polymer chains, so that the diffusing molecule produces the adequate space it needs for migrating through the polymer.

Meares¹⁵ supposed that the diffusion goes along a cylindrical volume proportional to $(\pi/4)d^{2\lambda}$ with d the diameter of the diffusing molecule and λ the length of the elemental jump distance. Meares and some other authors could observe a proportionality of ΔE and d^2 .^{15,16}

A plot of the ΔE values of the alkane diffusion in LDPE with the square of the radius qualitatively gives the same curve as the correlation of ΔE with $\Delta_v H_s$. Here we also get a curve consisting of two straight lines with a break point. Because the quality of the correlation is not as good as that of ΔE with $\Delta_v H_s$, this plot will not be shown here.

Lawson¹⁷ could demonstrate for the diffusion of small amounts of substances in polymers that $\Delta S^\ddagger/\Delta H^\ddagger = k \cdot \alpha$, with k a constant and α the thermal expansion coefficient. Because $D_0 = e \cdot \lambda^2 [(K \cdot T)/h] \exp(\Delta S^\ddagger/R)$ and λ changes to λ_{solv} for interdiffusion, the factor D_0 is essentially determined by $\Delta S^\ddagger/R$. Therefore, a correlation should exist between D_0 and ΔE or ΔH^\ddagger because $\Delta H^\ddagger = \Delta E - RT$. Figure 7 confirms this. Similarly to Figure 6, we get a curve of two straight lines of different slope.

Figures 6 and 7 show linear functional relations. Because $\Delta_v H_s$, as product of the boiling point and Trouton's constant is available for many alkanes, the diagram of Figure 6 will give the adequate ΔH^\ddagger and the diagram of Figure 7 the adequate D_0 . Thus a very exact estimation of diffusion coefficients of any alkanes at different temperatures for this polymer is possible.

TABLE III
Experimental Values of Temperature Dependence on Diffusion and Relative solubility

Alkane with <i>n</i> carbon atoms	Ethanol				Hexane			
	40°C	23°C	10°C	6°C	40°C	23°C	10°C	6°C
	<i>ln D</i>				<i>ln D</i>			
12	-18.26	-19.50	-20.89	-21.97	-14.57	-15.86	-16.64	-17.42
14	-18.49	-20.14	-21.06	-22.20	-14.82	-16.12	-17.01	-17.78
16	-18.72	-20.40	-21.57	-22.52	-15.10	-16.32	-17.38	-18.17
18	-19.03	-20.68	-22.16	-22.95	-15.35	-16.63	-17.77	-18.54
20	-19.42	-20.91	-22.70	-23.61	-15.64	-17.03	-18.23	-18.97
22	-19.86	-21.50	-23.32	-24.43	-15.94	-17.55	-18.70	-19.47
24					-16.17	-18.02	-19.26	-20.06
26					-16.58	-18.63	-19.85	-20.65
28					-16.90	-19.04	-20.45	-21.36
30					-17.14	-19.66	-21.15	-22.07
32					-17.37	-20.63	-21.67	-22.70
	<i>ln S_r</i>				<i>ln S_r</i>			
12	0.062	-0.03	0.067	0.10	-1.42	-1.43	-1.35	-0.98
14	0.25	0.26	0.21	0.26	-1.41	-1.51	-1.26	-0.90
16	0.52	0.47	0.70	0.56	-1.41	-1.43	-1.17	-0.85
18	0.83	0.92	1.41	1.01	-1.38	-1.20	-1.06	-0.77
20	1.28	1.44	1.75	1.62	-1.32	-1.14	-0.90	-0.64
22	1.78	2.09	2.47	2.42	-1.26	-0.89	-0.71	-0.47
24					-1.18	-0.94	-0.44	-0.23
26					-1.05	-0.73	-0.09	-0.11
28					-1.02	-0.42	0.15	0.39
30					-0.81	-0.031	0.68	0.86
32					-0.81	0.26	0.82	0.97

TABLE IV
 Activation Energies ΔE and Arrhenius Preeponential Factors D_0 of Diffusion of Alkanes in Swollen (Hexane as Solvent) and Nonswollen (Ethanol as Solvent) LDPE

Alkane with <i>n</i> carbon atoms	Hexane		Ethanol	
	ΔE (kcal)	$\ln D_0$	ΔE (kcal)	$\ln D_0$
12	13.65	7.4	18.03	10.89
14	14.30	8.21	17.61	9.86
16	15.00	9.10	18.64	10.99
18	15.65	9.89	19.55	12.47
20	16.42	10.82	21.00	14.52
22	17.35	11.98	22.59	16.64
24	19.13	14.58		
26	20.00	15.53		
28	21.94	18.36		
30	24.32	21.88		
32	25.69	23.68		

For example we get from the diagram of Figure 6 for the alkane C_6H_{14} a ΔH^\ddagger of 10,300 cal ($T_s = 68.9^\circ\text{C}$, $\Delta_v H_s = (273 + 68.9) \cdot 21.5/4$ cal), which gives for ΔE a value of 10888 cal at 25°C . Going into the diagram of Figure 7 this value corresponds to a $\ln D_0$ of 3.5. This leads to $D = 3.0 \times 10^{-7}$ cm^2/s for the diffusion coefficient of hexane in LDPE. Peeters et al.¹⁸ have found a value of 3.8×10^{-7} cm^2/s for the diffusion coefficient of hexane in LDPE determined by permeation experiments with pure hexane.

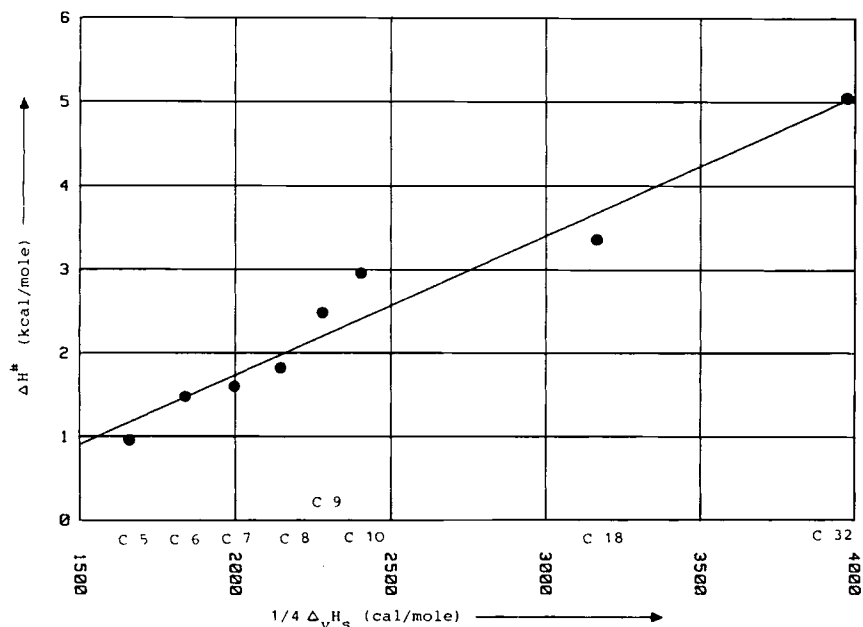


Fig. 5. Correlation of the activation enthalpies ΔH^\ddagger of the alkanes vs. the heats of vaporization for the self diffusion of the *n*-alkanes, data taken from Douglas and McCall.¹⁴

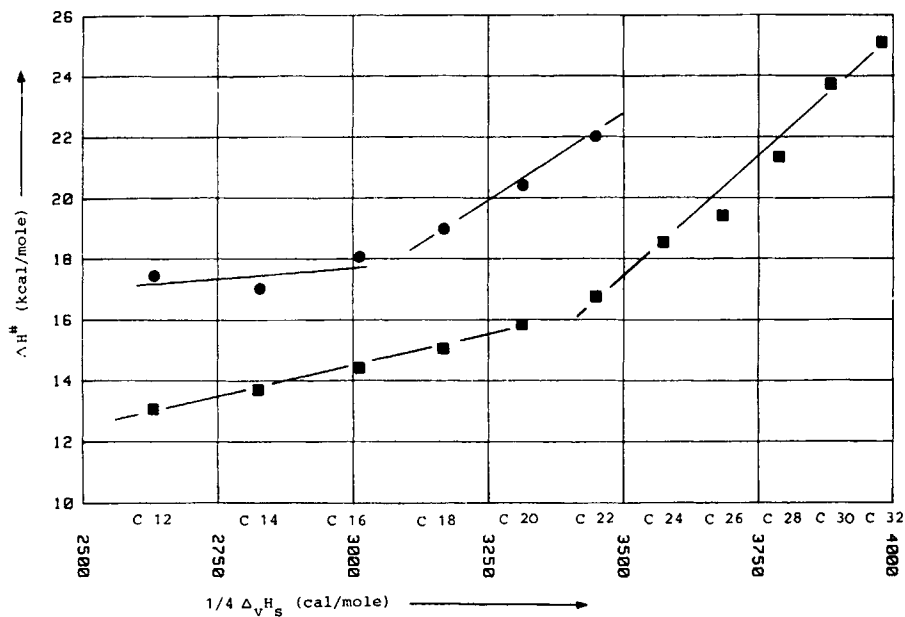


Fig. 6. Correlation of the activation enthalpies ΔH^\ddagger of the alkanes vs. the heats of vaporization $\Delta_v H_s$ of the alkanes for the diffusion in swollen (lower curve, hexane as solvent) and nonswollen LDPE (upper curve, ethanol as solvent).

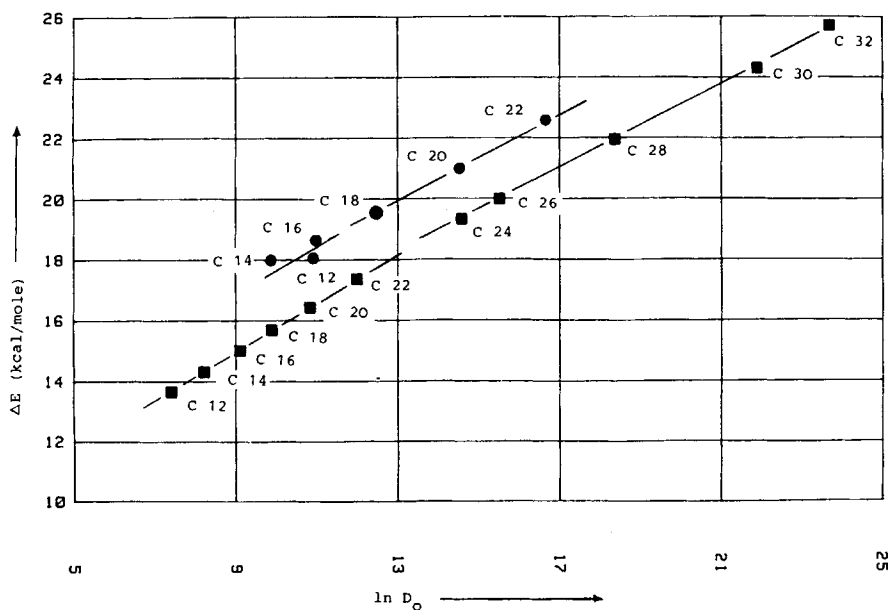


Fig. 7. Correlation of the activation energies ΔE of the alkanes vs. the Arrhenius pre-exponential factors D_0 of the alkanes for the diffusion in swollen (lower curve, hexane as solvent) and nonswollen LDPE (upper curve, ethanol as solvent).

Solubility Constant

As stated at the beginning, we have determined the relative solubility constants S_r (partition coefficients) on account of practical reasons to avoid the determination of the partial pressures of the single components over the solution. A disadvantage of these constants is their solvent dependance (Table II).

Analogous to the log/log plot of the diffusion constants, we can mutually correlate the relative solubility constants.

The diagram of Figure 8 shows the relative solubility constants of the alkanes as an example where ethanol served as solvent. The diagram shows that the relative solubilities of LDPE and HDPE are very similiar, whereas that of PP differs a little. We have no explanation for this effect at the moment because the absolute solubility normally decreases with growing crystallinity. It is known that the absolute solubility in HDPE is lower than in LDPE.¹⁹

The increase of the relative solubility constant S_r with increasing carbon number both for hexane, acetone, and ethanol as solvents is a consequence of the growing interaction between alkane and solvent moleule, leading to an increase of the activity coefficient and therefore of the pressure over the solution.

Temperature Dependence of the Solubility Constant

Figure 9 shows the temperature dependence of the relative solubility constants of the alkanes in LDPE (Table III), where ethanol served as solvent. The higher alkanes follow a Gibbs-Helmholtz relationship with

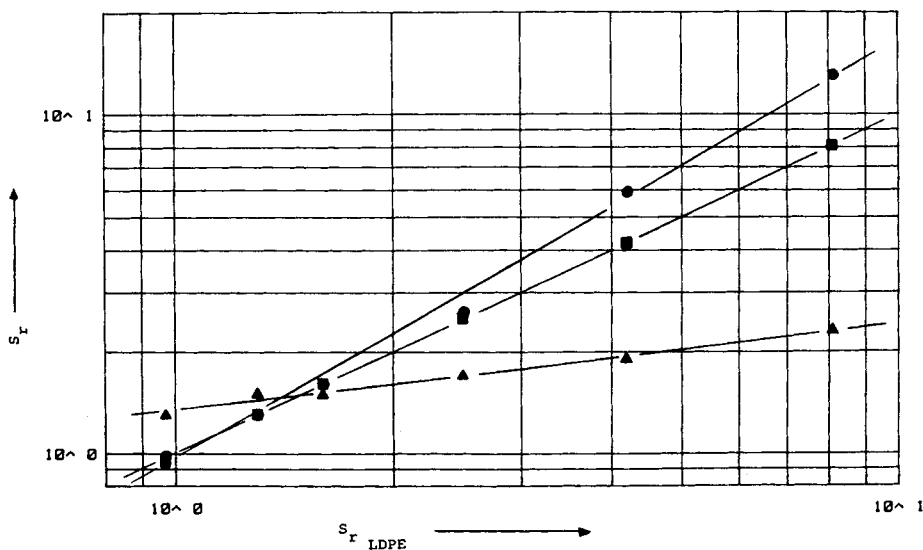


Fig. 8. Correlation of the relative solubility constants of the alkanes dissolved in ethanol in LDPE (■), HDPE (●), and PP-homopolymer (▲) as function of the relative solubility constants of the alkanes in LDPE.

$\Delta H_{\text{solution}}$ constant whereas the lower ones seem to show not such a marked or even no dependence of such a relationship. We find the same behavior for the temperature dependence of the relative solubility constants of the alkanes in LDPE with hexane as solvent.

An explanation for this behavior results from the distinct opposite directed values in S_r ; because of the definition of $S_r = c_p/c_i = (S \cdot p^0 \cdot M_s \cdot \gamma / \rho_s)$, it follows that the relative solubility constants contain four temperature-dependent values p^0 , γ , S , and ρ , whereby the temperature dependence of ρ is surely negligible. Therefore, it could be possible that the influence of the temperature dependence of the activity coefficient predominates at the higher alkanes, perhaps leading to straight lines with positive slopes whereas at the lower chained alkanes the influence of the temperature dependence of the vapor pressure predominates, leading to lines with negative slopes. Interpreting the temperature dependence of the relative solubility (partition) constants in thermodynamic terms by introducing the chemical potential, we find that $d \ln S_r / dT = (H_{\text{polym}}^0 - H_{\text{solv}}^0) / RT^2$, which means that the different slopes we find in the diagram of Figure 9 are caused by the difference of the heat of solution of the alkanes in the polymer H_{polym}^0 and liquid phase H_{solv}^0 . Changing the temperature, the heats of solubility seem to change, too; therefore, it is obvious that a correlation of T_s or $\Delta_v H_s$ with $\ln S_r$ or ΔE_{S_r} cannot give such a correlation as in the case of D or $\Delta_v H_s$ because of these superposing effects.

In contrast to this a correlation of T_s with $\ln S$, the logarithm of the absolute constant, should be possible, because now we have no superposing

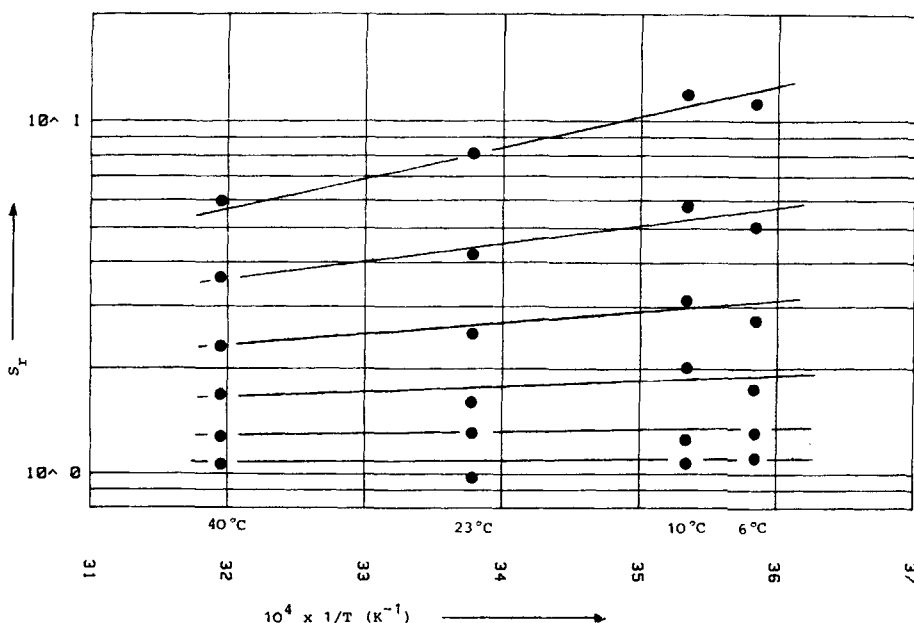


Fig. 9. Temperature dependence of the relative solubility constants of the n -alkanes for LDPE, alkanes dissolved in ethanol; curves in the turn from above: alkanes with 22, 20, 18, 16, 14, and 12 carbon atoms; S_r relative solubility constant, T absolute temperature.

effects. Such correlations are known for gases and highly volatile organic compounds.²⁰

Molecular Weight Dependence

Cratin²¹ supposed that the partial molar free energy of a molecule when partitioning between water and an organic solvent is the sum of a lipophilic component μ_L and n hydrophilic groups μ_H of the molecule for each solvent. With this assumption he derived the following equation for the partition coefficient P :

$$RT \ln P = n\Delta\mu_H^0 + \Delta\mu_L^0 + RT \frac{\bar{V}_1}{\bar{V}_2} \quad (19)$$

where $\Delta\mu_H^0$ and $\Delta\mu_L^0$ are the differences of the partial molar free energies of the hydrophilic and lipophilic part of the molecule in the two solvents and the \bar{V} are the corresponding molar volumes of the two solvents. The validity of this equation has been demonstrated by Cratin by plotting the partition data of $p\text{-C}_8\text{H}_{15}\text{C}_6\text{H}_5\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{-CH}_2\text{CH}_2\text{OH}$ with n varying from 1 to 10.

Analogous to this, the equation above should become

$$RT \ln P = n\Delta\mu_L^0 + \Delta\mu_H^0 + RT \ln \frac{\bar{V}_1}{\bar{V}_2} \quad (20)$$

if varying the lipophilic parts of a molecule and keeping the hydrophilic part constant.

The diagram of Figure 10 where the data of straight chained carboxylic acids $\text{H}-(\text{CH}_2)_n-\text{CO}_2\text{H}$ have been plotted illustrates the validity of this assumption. We have taken this example because data of alkanes partitioned between two immiscible organic solvents are not available. Therefore, if partitioning the alkanes between a polymer and a liquid, there should exist a similar relation because we are able to make the same considerations. Taking into account that an aliphatic hydrocarbon has no hydrophilic component, the following equation should be valid:

$$RT \ln S_r = n\Delta\mu_L^0 + RT \ln \frac{\bar{V}_1}{\bar{V}_2} \quad (21)$$

where now $\Delta\mu_L^0$ is the difference of the partial molar free energy of the lipophilic unit in the polymer and the liquid, respectively. Hence, plotting $\ln S_r$ vs. the number of the carbon atoms, the diagram should yield a straight line.

Figure 11 shows the data of the alkanes partitioned between LDPE and hexane exemplarily. If Cratin's assumptions concerning the activity of the lipophilic or hydrophobic units are right as the data of the carbon acids

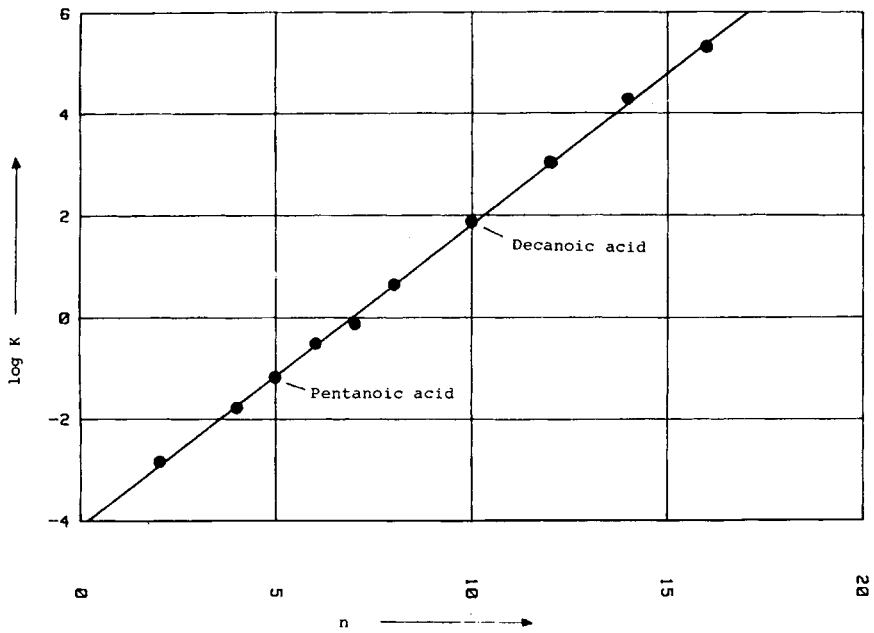


Fig. 10. Correlation of the logarithms of the partition coefficients of carboxylic acids versus the number of the carbon atoms for the partition between water and hexane,²² heptane,^{23,24} or octane.²⁵

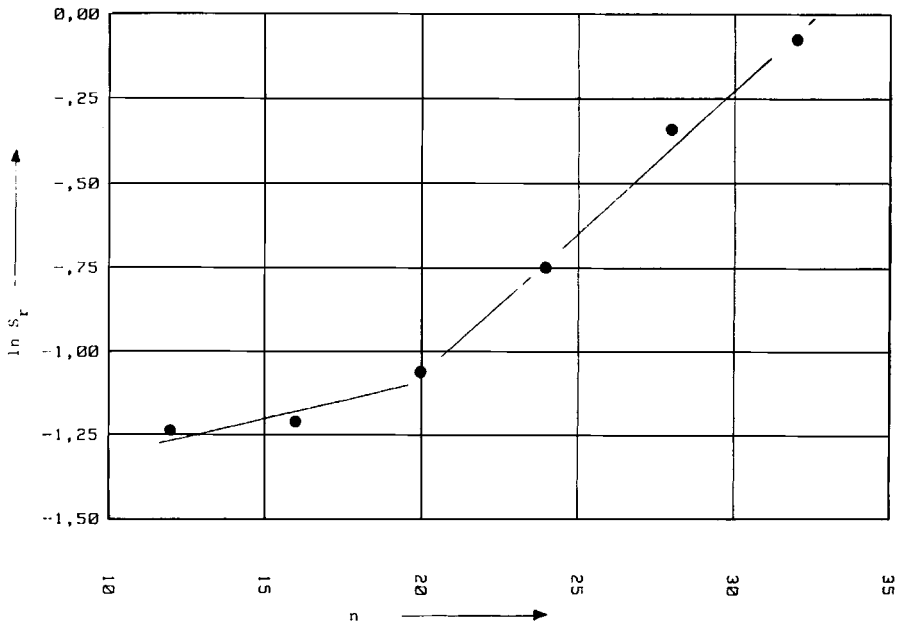


Fig. 11. Correlation of the logarithms of the relative solubility constants of alkanes vs. the number of carbon atoms of the alkanes for the partition between LDPE and hexane.

seem to corroborate, the two lines of the slopes would indicate that the solubility mechanism of the higher alkanes in the polymer differs from that of the lower chained ones which may be caused again by the holes or the free volume in the polymer.

CONCLUSION

The diffusion and relative solubility constants (partition coefficients) of *n*-alkanes in the polyolefines LDPE, HDPE, and PP have been measured by a permeation method, where the permeation of the permeate out of a solution through the polymer into a solution which at the beginning of the experiment has been free of permeate has been measured. It is shown that the activation energy ΔE for the diffusion in the polyolefines is growing with increasing carbon number.

There exist correlations between the activation energies ΔE and the heats of vaporization $\Delta_v H_s$ and between the Arrhenius preexponential factors D_0 . These correlations are valuable for the estimation of the diffusion coefficients of *n*-alkanes.

Furthermore, these results show that higher molecular substances are able to permeate from a solution staying in contact with a polymer. The driving force of this process is the vapor pressure over the solution of the dissolved substances. To avoid vapor pressure measurements, relative solubility constants (partition coefficients) have been used.

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