

THERMODYNAMICS OF THE ABSORPTION OF HYDROCARBON VAPORS IN POLYETHYLENE FILMS

E.F. CASTRO, E.E. GONZO* and J.C. GOTTIFREDI

Instituto de Investigaciones para la Industria Química (INIQUI), Universidad Nacional de Salta, CONICET, Buenos Aires 177, (4400) Salta (Argentina)

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Summary

Solubility of n-butane, n-pentane, n-hexane and n-heptane vapors in polyethylene membranes was measured with an accurate gravimetric technique as a function of temperature, within the range of 258 to 318 K, and relative vapor pressure of hydrocarbons (up to 0.95). The results are analyzed with the scope of establishing a unique expression to predict the solubility of the hydrocarbon vapors. It is shown that such an expression exists and can be used with a fair degree of accuracy to estimate both solubility and solubility coefficients, in spite of the marked deviation of the experimental results from Henry's law. The effect of temperature over the whole range investigated is also well correlated, and the isoplethic heat of absorption was calculated, showing that its values are independent both of temperature and solubility. The Flory-Huggins theory was also used to analyze experimental results and the values of the interaction parameter were calculated, which can be used in turn to predict solubility and solubility coefficients of hydrocarbon vapors.

Introduction

Permeation of gases and vapors through polymeric films has been the main subject of many contributions in the recent literature [1-3], mainly due to its increasing importance in separation processes and applications in the food industry [4-6]. It is well established that permeability is the result of a combination of solubility and diffusion phenomena. Prediction of permeability coefficients is of primary interest and can only be achieved based on knowledge of the corresponding solubility and diffusivity coefficients.

The present contribution presents a study aimed at establishing a general expression for the solubility and solubility coefficients of four hydrocarbons (namely n-butane, n-pentane, n-hexane and n-heptane) in polyethylene as a function of temperature and pressure within the range 258 to 318 K and up to

*To whom correspondence should be addressed.

a relative pressure (p/p°) of 0.95, normalized with respect to the vapor pressure of the pure compound (p°).

Since the solubility data of these organic vapors in polyethylene deviate markedly from Henry's law, the solubility coefficients are functions not only of temperature but also of pressure. Thus, an attempt to correlate the experimental findings as a function of molecular weight of the hydrocarbon, temperature and relative pressure is presented, which produces very accurate results when compared with experimental values (maximum deviation under more unfavorable conditions being 18%).

Temperature dependence of solubility is also analyzed over the whole range of temperatures investigated. A method is presented to deduce the heat of mixing of penetrant and polymer after calculation of the isoplethic heat of absorption (q_{iso}), showing that q_{iso} values are independent of temperature and solubility.

Using the Flory-Huggins theory the interaction parameter (χ) is obtained, showing that in the whole range of variables investigated the parameter can be considered as constant. Consequently, the deduced value of χ can be used to predict the solubility and solubility coefficient with great accuracy.

It must be pointed out that in our analysis it was assumed that the amorphous polymer phase is the only part of the structure responsible for the solubility and diffusion phenomena [7,8]. A degree symbol ($^\circ$) will be used throughout the paper to indicate data expressed per mole of penetrant and a subscript asterisk (*) to indicate that the basis is grams of amorphous polymer.

Experimental

Materials

The properties of the polyethylene films used in the experiments were as follows: Low density polyethylene, density $\rho_p = 0.9157 \text{ g/cm}^3$ at 30°C . Density was determined by pycnometry according to the ASTM D 792-66 method. Average thickness was $2.5 \times 10^{-5} \text{ m}$. The volume fraction of amorphous polymer was $\alpha = 0.57$ at 30°C . It was estimated from the density assuming crystalline- and amorphous-phase specific volumes of 1.003 and $1.171 \text{ cm}^3/\text{g}$, respectively, according to the expression given by Michaels and Bixler [8]. It was also verified through thermal analysis using a differential scanning calorimeter (Perkin-Elmer DSC-2C). The heat of fusion of the film was $\Delta H_m = 29.3 \text{ cal/g}$. The nominal average molecular weight was $M_n = 24900 \text{ g/mol}$ with a branching index of 3, as determined by GPC chromatography.

Chromatoquality (Merck) n-pentane, n-hexane and n-heptane were used without further purification; 98% n-butane was dried before use.

Apparatus and procedure

The absorption isotherms were measured in an apparatus which is shown schematically in Fig. 1. A Cahn RG electrobalance was used to monitor the

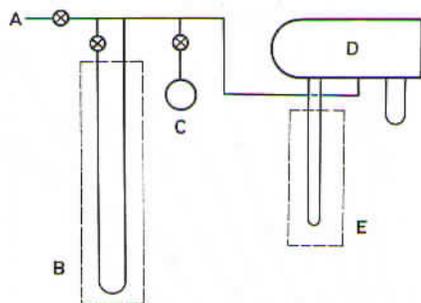


Fig. 1. Schematic representation of the experimental set-up. A: vacuum line; B: manometer; C: solvent reservoir; D: high-vacuum electrobalance; E: constant-temperature bath.

weight change. The balance sample tube was immersed in a constant-temperature water bath controlled to within $\pm 0.1^\circ\text{C}$. The temperature was measured with a thermocouple in the vertical tube of the electrobalance to a point just above the center of the sample. Samples of about 100 mg of polyethylene films were used; the sensitivity of the balance was $1\ \mu\text{g}$.

All liquid solvents (n-pentane, n-hexane and n-heptane) were thoroughly degassed prior to use. Before starting a sorption run, the system containing the sample was completely evacuated. Then the penetrant vapor was admitted into the system until the desired pressure was obtained. The equilibrium pressure and the weight gain of the sample were measured after no further increase in weight, over a 2 hour period, was observed in the balance recorder. After that, more hydrocarbon vapor was admitted. This procedure was repeated until the maximum value of p/p° permitted by the experimental system was reached.

Upon completion of the sorption run, the penetrant was evacuated from the electrobalance to begin the desorption run. This was accomplished by opening and closing the vacuum valve.

Results and discussion

Isotherms

The absorption isotherms are shown in Figs. 2-5. They are curved upward, in all cases, similar in shape to type-III BET adsorption isotherms, which means that the solubility coefficients are temperature and concentration (pressure) dependent [9-11].

From the plot of solubility S (g penetrant/100 g polymer) versus relative pressure p/p° (Fig. 6) it can be seen that the isotherms are inverted with respect to temperature. Since the solubility increases with temperature at constant relative pressure, this is a clear demonstration that the mixing process, for all penetrants, is endothermic.

Figure 4 also shows the sorption and desorption data of n-hexane at 30°C

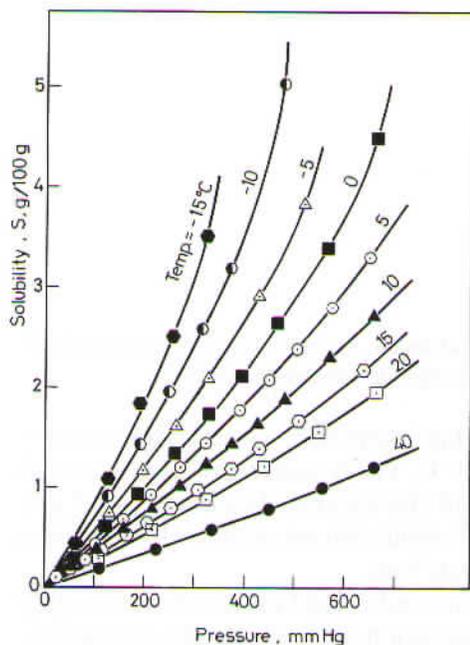


Fig. 2. Butane sorption isotherms in polyethylene.

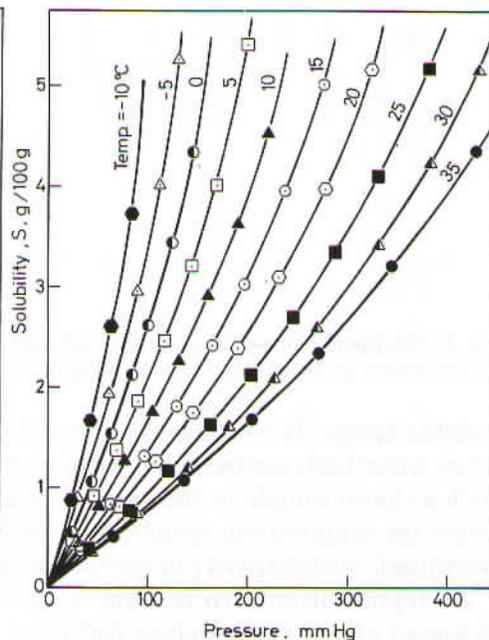


Fig. 3. Pentane sorption isotherms in polyethylene.

and a pressure up to 120 Torr ($p/p^\circ = 0.7$). All the experimental data points are well correlated by a single curve which reveals no detectable hysteresis. Since the solvent is sorbed only in the amorphous phase of the polymer, the sorption of penetrant must produce a deformation of the polymer structure and consequently result in strain of the phases of the polymer. In view of the results obtained, it is concluded that the phenomenon previously described is reversible.

Temperature dependence of solubility

As shown by Fig. 7, the temperature dependence of the solubility over the whole range of temperatures studied, obeys the relationship:

$$S = S' \exp(-B/T^2) \quad (1)$$

which means, from the thermodynamic point of view, that the apparent heat of solution is temperature dependent, i.e.

$$\Delta H_s = 2BR/T \quad (2)$$

where B and S' are constants, ΔH_s (cal/mol) is the apparent heat of solution, R is the gas constant and T the absolute temperature. The values of B for n-

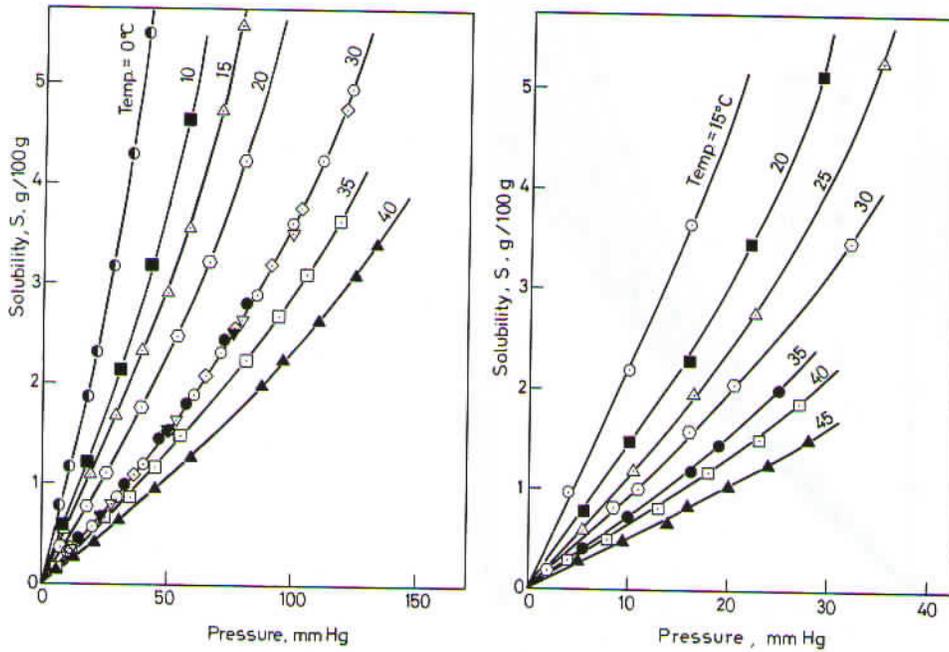


Fig. 4. Hexane sorption isotherms in polyethylene. Isotherm at 30 °C: filled points show desorption data.

Fig. 5. Heptane absorption isotherms in polyethylene.

butane, n-pentane, n-hexane and n-heptane are -3.64×10^5 , -4.62×10^5 , -5.66×10^5 and -5.91×10^5 K², respectively. The apparent heat of solution is found to be insensitive to total penetrant pressure. This behaviour is in agreement with previous findings by Stern et al. [12] for the solubility coefficients of twenty-eight gases and vapors.

The solvent heat of mixing was calculated from the experimental data by obtaining the isoplethic heat of absorption (q_{iso}), which is the difference in enthalpy between one mole of penetrant as a perfect gas at any pressure ($H_{1,g}$) and one mole of the gas absorbed in equilibrium with solvent vapor at pressure p ($H_{1,\text{sol}}$), according to:

$$\left(\frac{d \ln p}{dT}\right) S^* = \frac{q_{\text{iso}}}{RT^2} \quad (3)$$

with

$$q_{\text{iso}} = H_{1,g} - H_{1,\text{sol}} \quad (4)$$

By considering that in the dissolution process the solvent vapor first condenses on the polymer surface and is then solubilized, the heat of mixing (ΔH_1^M) can be calculated as

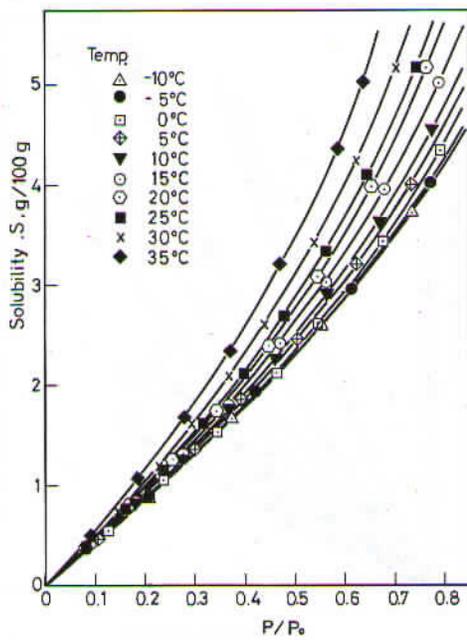


Fig. 6. Solubility of pentane in polyethylene at various temperatures as a function of the relative pressure.

$$\Delta H_1^M = -q_{\text{iso}} - \Delta H_1^c \quad (5)$$

where ΔH_1^c is the molar heat of condensation.

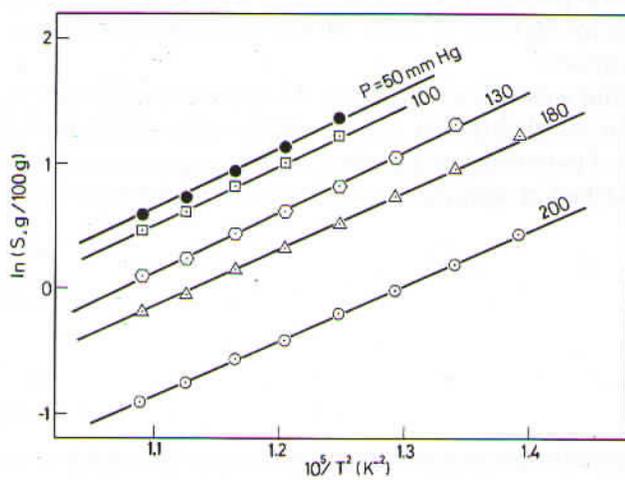


Fig. 7. Effect of temperature on pentane solubility in polyethylene.

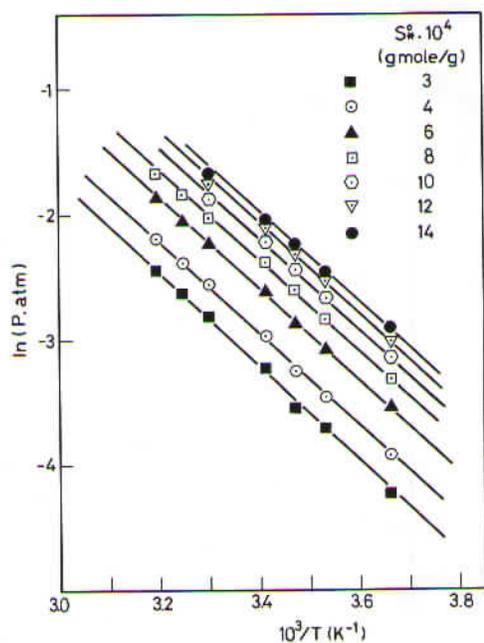


Fig. 8. Plots of $\ln p$ against reciprocal temperature for hexane at different S_0^* .

Figure 8 shows a plot of $\ln p$ versus $1/T$; the slope is equal to $-q_{\text{iso}}/R$. As can be seen, q_{iso} is always positive and independent of system composition (solubility) and temperature. We used this procedure to calculate the penetrant heat of mixing because the apparent heat of solution, ΔH_s , previously defined, is distributed in some unknown and complex manner between penetrant and polymer.

Table 1 shows values of q_{iso} for two of the solvents and the corresponding heat of mixing ΔH_1^M .

TABLE 1

Values of isoplethic heat of absorption and heat of mixing of n-pentane and n-hexane

Solvent	q_{iso} (cal/mol)	T (K)	ΔH_1^M (cal/mol)
n-Pentane	6369	273	388
		303	201
n-Hexane	7182	273	747
		303	422

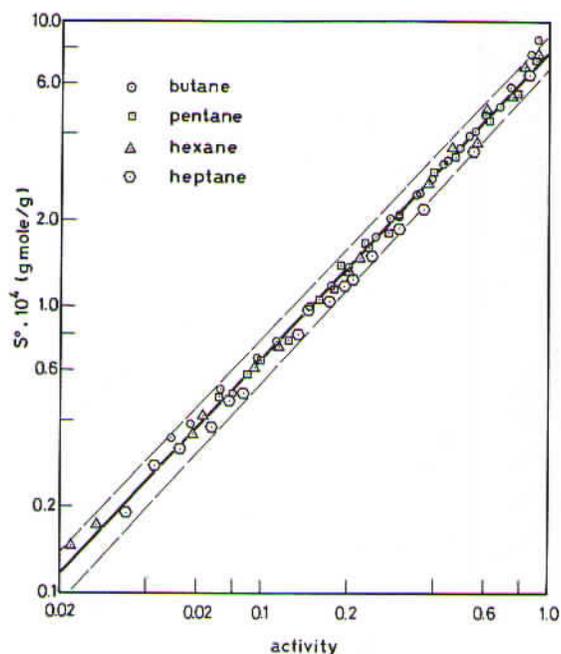


Fig. 9. Log-log plot of molar solubility versus solvent activity.

Solubility

With the aim of predicting the molar solubility per gram of total polymer (S°) for the different penetrants used, the solubility was plotted versus the solvent activity on a log-log scale (Fig. 9). The fugacity of pure solvent at experiment temperature was taken as the standard state for the activity (a_1) and the fugacity coefficients were calculated according to the Redlich-Kwong equation [13].

The correlation, a single equation for the four solvents at the 95% confidence level, is

$$S^{\circ} \text{ (mol/g)} = (7.91 \pm 1.03) \times 10^{-4} a_1^{(1.08 \pm 0.02)}; \quad (6)$$

it is valid for activities up to 0.9.

Solubility coefficient

The solubility data, corrected for the crystalline content of polyethylene, were fitted to an equation of the form:

$$S_*^{\circ} = C_1 p + C_2 p^3 \quad (7)$$

using the optimization program REGRE [14] to determine the values of the two parameters C_1 and C_2 at each temperature and over the entire range of pressures investigated. Starting from these equations, the solubility coeffi-

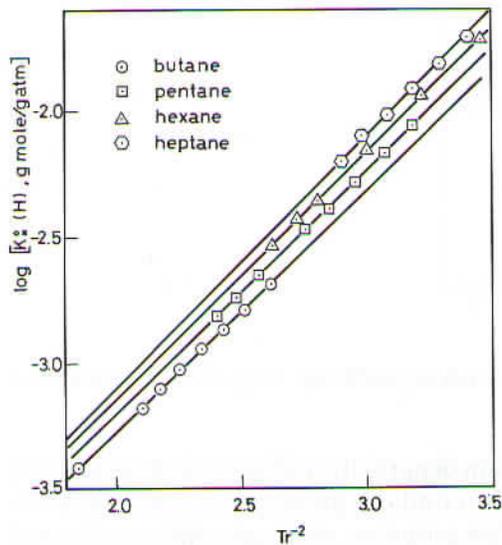


Fig. 10. Relation between the solubility coefficient (K_*°) and the reduced temperature in the Henry's law limit.

coefficients were obtained. Following the observations of Stern et al. [12], the logarithm of the solubility coefficient K_*° (mol/g amorphous polymer-atm) in the Henry's law limit ($p \rightarrow 0$) was plotted versus $(T_c/T)^2$, where T_c is the appropriate critical temperature (Fig. 10). A linear regression is found, whose parameters are also a linear function of the penetrant molecular weight. The solubility coefficients, in the Henry's law limit $K_*^{\circ}(H)$, are well correlated by the equation:

$$\log K_*^{\circ}(H) = (-5.265 + 2.03 \times 10^{-3} M_1) + (0.855 + 1.42 \times 10^{-3} M_1) T_r^{-2} \quad (8)$$

This equation predicts Henry's law solubility coefficients with a maximum deviation of 9% with respect to the experimental values. Extrapolating eqn. (8) to other saturated hydrocarbons it was found that it predicts quite well the experimental solubility coefficients as determined by several authors [8,11,15,16].

Since the slopes of the lines of $\log K_*^{\circ}$ versus T_r^{-2} for different values of p/p° , Fig. 11, remain constant, a full correlation for K_*° over the complete range of temperature and pressure values studied was obtained, which leads to the equation

$$\log K_*^{\circ} = (-5.265 + 2.03 \times 10^{-3} M_1) + (0.855 + 1.42 \times 10^{-3} M_1) T_r^{-2} + (-0.940 + 3.56 \times 10^{-2} M_1 - 2.296 \times 10^{-4} M_1^2) (p/p^{\circ}) \quad (9)$$

The deviations between predicted and experimental values are always less than 18%; the maximum difference is shown by n-heptane.

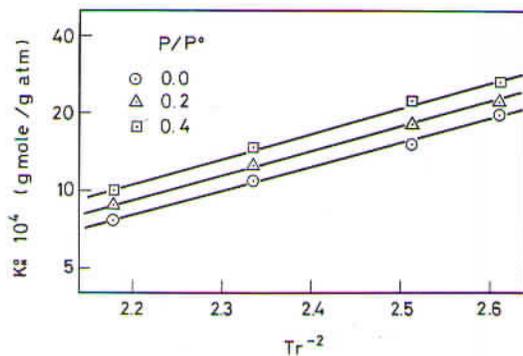


Fig. 11. Effect of reduced temperature on the solubility coefficient (K_*^c) at constant values of relative pressure.

In order to determine when the system departs from Henry's law behaviour, the solubility coefficient was analyzed to find the pressure (p_H) at which 5% deviation from Henry's law occurs. This criterion, although arbitrary, is used frequently [17,18], and in our case is reasonable, as pointed out by Stern et al. [12]. Taking into account the definition of the criterion to be used and considering that the solubility coefficient values increase with pressure, the 5% deviation will be reached when

$$K_*^c / K_*^c(H) = 1.05 \quad (10)$$

According to eqns. (9) and (10) it is found that

$$p_H = 0.0212 p^o / (-0.940 + 3.56 \times 10^{-2} M_1 - 2.296 \times 10^{-4} M_1^2) \quad (11)$$

As can be seen, the maximum pressure after which the departure from Henry's law becomes greater than 5% is a function only of penetrant saturation vapor pressure.

Solvent-polymer interaction parameter

The Flory-Huggins [19] interaction parameters χ for each of the systems studied were obtained from:

$$\ln a_1 = \ln v_1 + (1 - 1/x) v_2 + \chi v_2^2 \quad (12)$$

where a_1 is the solvent activity and x is the approximate number of segments per polymer chain. The volume fractions of polymer and penetrant, v_2 and v_1 , respectively, were calculated on the basis of the amorphous content of the polymer, as pointed out by Rogers et al. [11], since the crystalline regions of the polymer are physically inaccessible to the solvent molecules.

To calculate χ , the $1/x$ term in eqn. (12) was neglected since its contribution is insignificant because of the molecular weight of the polyethylene used and the high concentration of polymer, giving

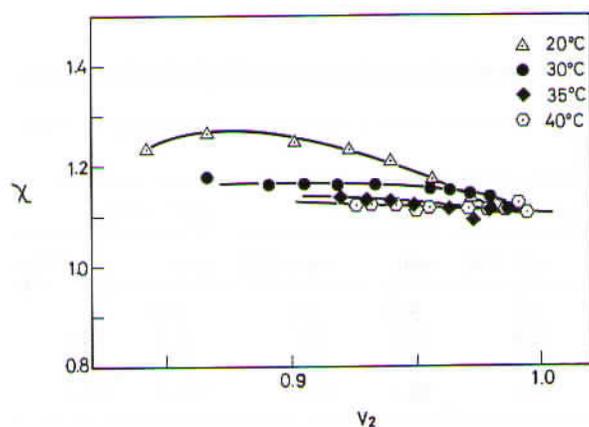


Fig. 12. The Flory-Huggins interaction parameter versus volume fraction of polymer at various temperatures. Penetrant: n-hexane.

$$\chi = [\ln (a_1/v_1 - v_2)]/v_2^2 \quad (13)$$

The volume fractions were calculated from the known densities of pure components, ρ_1 (liquid solvent) and ρ_p , and the volume fraction of amorphous polyethylene, α , by assuming that solvent and polymer volumes are additive on mixing.

The value of χ for any of the penetrants varies with v_2 , increasing as v_2 decreases, as shown by Fig. 12 for n-hexane. As a result of this constant variation, no single value of χ will be adequate to define the absorption over all of the solvent activity range. However, χ remains approximately constant (less than 5% variation) at temperatures greater than 303 K. With the mean value of χ at this high temperature it is possible to calculate the solubility and the solubility coefficient in the pressure range used in the experiments. Assuming ideal behaviour of the solvent vapors, $a_1 = p_1/p_1^\circ$, and eqn. (12) gives:

$$p_1 = p_1^\circ v_1 \exp [v_2 + \chi v_2^2] \quad (14)$$

$$S_*^\circ = v_1 \rho_1(\text{liq}) / \rho_{pa} M_1$$

$$S_*^\circ = p_1 \rho_1(\text{liq}) \exp [-v_2 + \chi v_2^2] / \rho_{pa} p_1^\circ M_1 \quad (15)$$

and

$$K_*^\circ = \rho_1(\text{liq}) \exp [-(v_2 + \chi v_2^2)] / \rho_{pa} p_1^\circ M_1 \quad (16)$$

where ρ_{pa} is the density of the amorphous phase of the polymer.

Table 2 shows the K_*° values calculated from eqns. (16) and (9), respectively. The agreement is good, although it is not possible to use Flory-Huggins theory for predicting absorption data in the range of temperatures studied since

TABLE 2

Comparison of the solubility coefficients determined experimentally and calculated using eqn. (16) for the four solvents studied

Solvent	T (K)	χ	$K_*^\circ \times 10^4$					
			$p/p^\circ = 0.1$		$p/p^\circ = 0.2$		$p/p^\circ = 0.3$	
			exp.	eqn. (16)	exp.	eqn. (16)	exp.	eqn. (16)
n-Butane	313	1.104	4.15	3.8	4.50	4.1	4.88	-
n-Pentane	308	1.058	14.1	13.8	15.6	14.7	17.2	16.0
n-Hexane	308	1.083	40.1	39.0	44.2	42.1	48.7	45.2
n-Heptane	313	1.065	87.3	86.6	94.1	90.4	101.4	96.2

the change of χ with concentration is particularly marked at low temperatures for the four systems studied. As an interesting feature, the value of χ at infinite dilution ($v_2 \rightarrow 1$) is almost identical, and equal to approximately 1.1, for the penetrants studied in the range of temperatures used. Therefore the solubility coefficient in the Henry's law region can be calculated using a unique expression: from equation (16) for $v_2 \rightarrow 1$

$$K_*^\circ(\text{H}) = \rho_1(\text{liq}) \exp(-2.1) / \rho_{\text{pa}} p_1^\circ M_1 \quad (17)$$

The difference between values of $K_*^\circ(\text{H})$ predicted by eqn. (17) and values determined experimentally (eqn. 8) are within 5%, with a maximum error of 10%, as shown in Table 3.

Conclusions

The present results are consistent with the pure absorption model, showing that the swelling of the glassy matrix of polyethylene polymer is reversible. In fact, it was clearly established that solubility results obtained by absorption and desorption processes with hydrocarbon vapors are not affected within the time scale of conventional sorption-desorption measurements. Nevertheless, results deviate markedly from Henry's law, indicating an important interaction between solute and substrate.

An analysis of the temperature dependence of solubility shows that the apparent heat of absorption is temperature dependent, as pointed out by Stern et al. [12]. However, the calculation of the isoplethic heat of absorption (q_{iso}) is clearly independent of both temperature and concentration of the absorbing species.

All the solubility data for the four hydrocarbons investigated can be fairly well correlated by a unique expression in terms of the activity coefficient of the hydrocarbon, and the solubility coefficient in terms of reduced temperature,

TABLE 3

Comparison of the solubility coefficients in the Henry's law region determined experimentally and calculated using eqn. (17) for the four solvents studied

Solvent	T (K)	$K_s^*(H) \times 10^4$	
		exp.	eqn. (17)
n-Butane	313	3.82	3.84
	293	6.71	6.99
	273	13.39	14.05
n-Pentane	308	12.75	12.75
	293	21.83	22.01
	273	51.56	50.69
n-Hexane	308	36.34	36.69
	293	68.98	69.10
	283	112.05	110.45
n-Heptane	313	81.06	79.56
	298	164.22	161.04
	288	279.88	271.11

pressure and molecular weight of the absorbing species. The limit where Henry's law can be applied is also established.

Flory-Huggins theory can be applied to find the interaction parameters, showing that its values remain fairly constant for temperatures greater than 300 K. This opens an alternative route to estimate solubility and solubility coefficients.

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