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SOLUBILITY OF LIQUID HYDROCARBONS IN POLYETHYLENE MEMBRANES

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Abstract

A novel procedure have been established to estimate, accurately, the solubility of liquid hydrocarbons in polyethylene membranes. This method is more precise than the experimental existing techniques and is based on the particular behavior of the hydrocarbon vapor solubility with temperature. A general expression, obtained by corresponding state approach which permits solubility of liquid *n*-hydrocarbons estimation, is presented. It is also shown that the apparent heat of mixing is temperature dependent while total pressure does not affect the solubility of liquid hydrocarbons.

Introduction

In view of the interest in the application of polymeric films to separate liquid mixtures by permeation [1-5], it appears necessary to determine the parameters that characterize transport across a membrane. The solubility of a liquid penetrant in a membrane is very important in predicting its pervaporation rate and for membrane selection purposes.

In this study, experimental methods normally used to measure liquid solubility in polymeric membranes were critically analized [6,7] and a new method was developed. This new procedure has the advantage of being simpler and more reliable than the usual techniques described in the literature. With this method solubilities of liquid hydrocarbons in polyethylene are estimated by extrapolation of vapor solubility data recently published [8] on the basis of the particular behavior of vapor solubility as a function of reduced temperature (T_r). Liquid solubility data obtained by this procedure agree within experimental error with data obtained by the traditional technique. Moreover it can be concluded, that the new method proposed in this contribution is the most accurate and permits clearly ascertain the effect of temperature on solubility as well as to deduce other important thermodynamic properties, such as heat of mixing.

Furthermore, a general expression for estimating solubility of liquid normal hydrocarbons in polyethylene as a unique function of reduced temperature and penetrant molecular weight is presented. This expression can be extremely usefull for predicting membrane selectivity behavior.

Experimental

Materials

The properties of the polyethylene films used in the experiments were as follows: low density polyethylene [8], density ρ_p = 0.9157 g/cm^3 at 30°C. Density was determined by pycnometry according to the ASTM D 792-66 mathod. Average thickness was 2.5 X 10^{-5} m. The volume fraction of amorphous polymer was α = 0.57 at 30°C. It was estimated from the density assuming crystalline –and amorphous– phase specific volumes of 1.003 and 1.171 cm^3/g, respectively, according to the expression given by Michaels and Bixler [9]. It was also verified through thermal analysis using a differential scanning calorimeter (Perkin-Elmer DSC-2C). The heat of fusion of the film was ΔHm = 29.3 cal/g. The nominal average molecular weight was M_n =

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24900 g/mol with a branching index of 3, as determined by GPC chromatography [8].

Chromatoquality (Merck) *n*-pentane, *n*-hexane, *n*-heptane and *n*-octane were used without further purification.

Apparatus and procedure

The experimental procedure used to obtain solubilities of hydrocarbon vapors were presented elsewhere [8]. As an example, Figure 1 shows the absorption isotherms for *n*-pentane vapors. For the other hydrocarbons the diagrames are similar and can be obtain from reference [8].

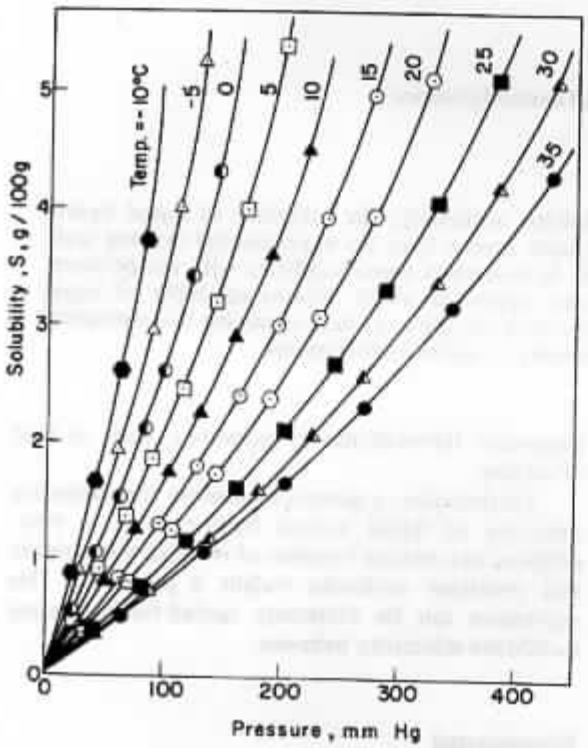

Fig. 1.– Pentane sorption isotherms in polyethylene.

Liquid hydrocarbon solubilities were measured using different experimental techniques described in the literature [6, 7]:

Technique A: Polyethylene discs of approximately 100 mg were soaked in liquid *n*-pentane, *n*-hexane and *n*-heptane, in a constant temperature bath for sufficient time to reach equilibrium. When the samples were removed from the liquid phase, the film surface was freed of adhering liquid by placing it between two sheets of filter paper for a short time and then weighed on an electronic analytical balance. The solubility was calculated by the gain in weight of the sample.

Technique B: The first step of this technique is like the previously cited, but after the sample was freed of adhering liquid a chronometer was started. The sample was weighted and the weight loss was recorded at fixed intervals. Plotting weight loss versus the square root of time (t), a straight line is obtained. When extrapolated to $t = 0$, the real weight gain for the sample can be calculated.

Results and discussion

In a previous work carried out by the authors [8], solubility of different hydrocarbon vapors in polyethylene membrane was measured with an accurate gravimetric technique within the temperature range of 258 to 318 K, and relative vapor pressures (P/Po) up to 0.95. The absorption isotherms were convex with respect to the pressure axis, similar in shape to type III BET isotherms, and tend to be asymptotic as P/Po → 1. Thus it is practically impossible to extrapolate the isotherms to P/Po = 1 to obtain the liquid hydrocarbon solubility.

Nevertheless, it was found that the logarithm of the solubility along an isobar, is a linear function of the inverse of the square of absolute temperature. Taking advantage of this system's behaviour, the new technique was developed.

When the logarithm of the vapor solubility is plotted as a function of $1/T_r^2$, at a given pressure, a straight line is obtained. By extrapolating this line to the temperature where the pressure of the isobar corresponds to that of vapor saturation, the solubility of the liquid is determined. This procedure is shown in Figures 2 and 3 for *n*-pentane and *n*-hexane, respectively. The figures also show that the logarithm of the liquid hydrocarbon solubility in polyethylene is a linear function of $1/T_r^2$ with a negative slope. Thus solubility of liquid hydrocarbons (S_L) increase with temperature (endothermic process), in accordance with previous findings of several authors [7, 10, 11].

The agreement between liquid solubility data, obtained by the extrapolation technique and direct experimental measurements (techniques A or B) is fairly good.

The precision of the experimental techniques described in this paper is not as good as the accuracy of the gravimetric method used in vapor absorption measurements. An error analysis on a solubility determination by any of the techniques A or B showed that the precision of the data obtained was ± 15% at the 95% confidence level. In general, technique B gives values of S_L a little higher than the other. Furthermore, due to the precision of the techniques A or B and since the effect of temperature on S_L is small, it is difficult to obtain the temperature dependence of S_L through these experimental methods, at least over the temperature range studied in this work.

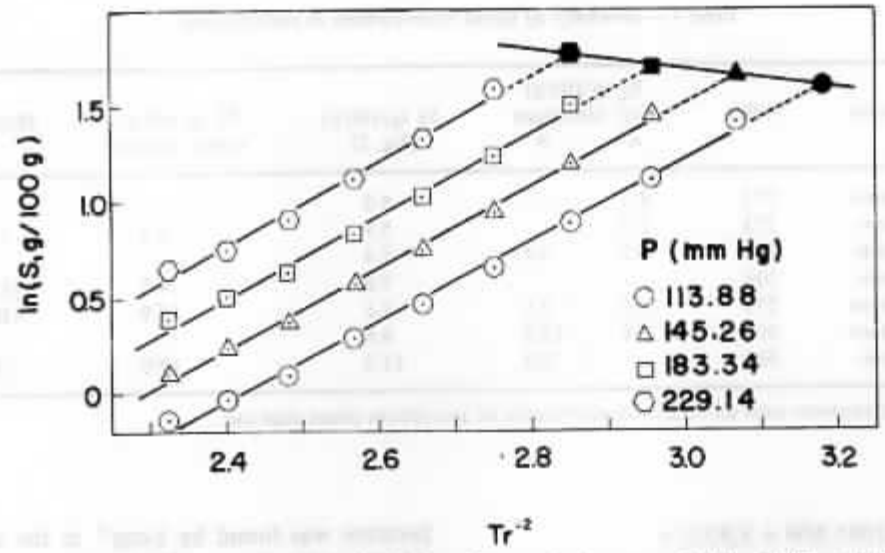

Fig. 2.– Solubility of n-pentane in polyethylene. Open symbols: vapor solubility. Filled symbols: liquid solubility.

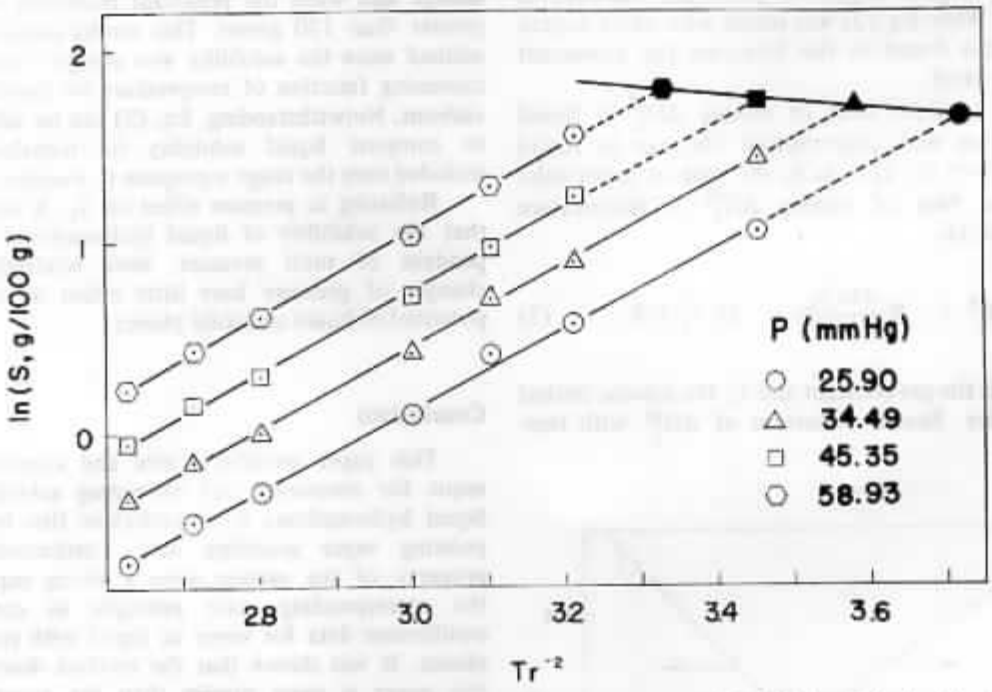

Fig. 3.– Solubility of n-hexane in polyethylene. Open symbols: vapor solubility Filled symbols: liquid solubility.

In Table 1 a comparison between values of S_L obtained with experimental procedures A or B and those found by the new method is shown.

To predict S_L values for other *n*-hydrocarbons, a general correlation of the form:

$$\ln S_L = a(MW) + b(MW)\,T_r^{-2} \qquad (1)$$

was developed as function of reduced temperature (T_r) and penetrant molecular weight (MW) using the corresponding state approach.

Taking into account liquid solubility data for *n*-butane, *n*-pentane and *n*-hexane, obtained by the procedure just developed, the parameters *a* and *b* of Eq. (1) were determined (see Fig. 4) leading to the following Eq.:

Table 1.– *Solubility of liquid hydrocarbons in polyethylene*

Penetrant	T(K)	S_L (g/100 g) Exp. technique A	B	S_L (g/100 g) (Eq. 2)	S_L^* (g/100 g) (other authors)	(Ref.)
n-pentane	273	4.7	–	5.3	–	–
n-hexane	273	5.2	–	5.9	5.3	(7)
n-hexane	303	6.7	9.4	7.4	–	–
n-hexane	308	–	–	7.6	4.3	(12)
n-heptane	273	6.0	8.1	7.6	16.9	(10)
n-heptane	303	9.9	12.6	8.8	–	–
n-octane	303	–	8.9	11.2	17.0	(10)

* Polyethylenes with different volume fraction of amorphous phase than our.

$$\ln S_L = (-0.01085\,MW + 3{,}904) + (0.01035\,MW - 1{,}238)\,T_r^{-2} \qquad (2)$$

where S_L is given in gram of penetrant/100 gram of polymer. When Eq. (2) was tested with other experimental data found in the literature the agreement was fairly good.

The apparent heat of mixing ΔH_L^M of liquid hydrocarbon with polyethylene film can be found directly from Eq. (1). As in the case of vapor solubility the heat of mixing ΔH_L^M is temperature dependent, i.e.:

$$\Delta H_L^M = -R\frac{d\ln S_L}{d(1/T)} = -2R\,T_c^2\,b/T. \qquad (3)$$

where R is the gas constant and T_c the solvent critical temperature. Similar behaviour of ΔH_L^M with temperature was found by Long[6] in the case of liquid *n*-heptane in polypropylene.

Due to the dependence of parameter *b* on penetrant molecular weight, ΔH_L^M should apparently change sign when the penetrant molecular weight is greater than 120 g/mol. This results cannot be explained since the solubility was always found as an increasing function of temperature for liquid hydrocarbons. Notwithstanding, Eq. (2) can be safely used to compute liquid solubility for *n*-hydrocarbons included over the range *n*-propane to *n*-octane.

Referring to pressure effect on S_L, it was found that the solubility of liquid hydrocarbons is independent of total pressure, since relatively small changes of pressure have little effect on chemical potential of liquid and solid phases.

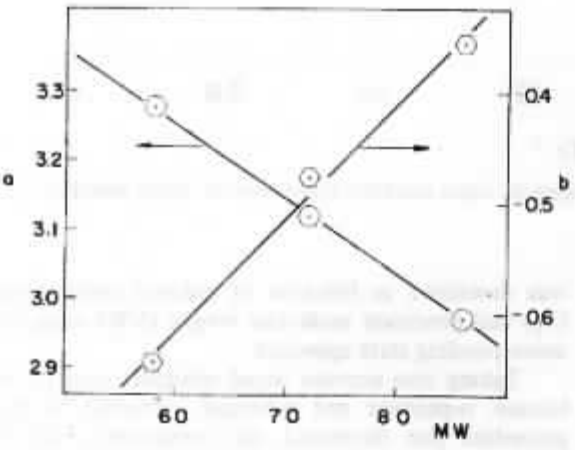

Fig. 4.– Parameters "a" and "b" of Eq. (1) as a function of penetrant molecular weight.

Conclusions

This paper provides a new and accurate technique for measuring and estimating solubilities of liquid hydrocarbons in polyethylene film by extrapolating vapor solubility data. Furthermore, this property of the system gives a strong support to the corresponding state principle in correlating equilibrium data for vapor or liquid with polymeric phases. It was shown that the method described in this paper is more precise than the experimental techniques generally used.

The analysis of temperature dependence of S_L shows that, as in the case of vapor solubility, the apparent heat of solution is temperature dependent.

The solubility of liquid hydrocarbons is well correlated by an unique expression in terms of reduced temperature and molecular weight of the solvent which is able to fairly well predict results previously reported in the literature.

It was found that S_L is pressure independent, at least for total pressure up to 2.5 atmospheres.

Resumen

Se establece un nuevo procedimiento para estimar, con exactitud, la solubilidad de hidrocarburos líquidos en membranas de polietileno. Este método es más preciso que las técnicas experimentales existentes y se basa en el comportamiento particular que tiene la solubilidad de los hidrocarburos gaseosos con la temperatura. Se presenta una expresión general, obtenida a través del principio de los estados correspondientes, la cual permite estimar la solubilidad de los hidrocarburos líquidos. Se demuestra, además, que el calor aparente de mezcla depende de la temperatura, mientras que la presión total no afecta la solubilidad de estos líquidos.

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