Vapor Sorption Characteristics of Condensable Hydrocarbon Vapor in Low-Density Polyethylene

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Synopsis

Sorption characteristics of vapors of pure hydrocarbon and their binary mixtures in low-density polyethylene were studied under various conditions of temperature and pressure. A new apparatus devised and utilized for the determination of composition of sorbed vapor in case of binary mixtures is described. The study demonstrates the effect of the presence of one component within the polymer on the sorption of another and also the occurrence of selectivity in sorption.

INTRODUCTION

Sorption of condensable hydrocarbon vapor in low-density polyethylene, particularly of binary mixtures, have not been studied in detail. Consequently, experimental determination of rate of sorption up to equilibrium for pure compounds (e.g., toluene, heptane, methylcyclohexane, and isooctane) and their binary mixtures (Tol-Mch, Tol-Hep, Tol-iOct, Hep-iOct) have been made. The range of temperature covered is 30 to 50°C and of pressure, 10 mm Hg to slightly below the respective saturation pressures.

The sorption equilibrium of binary vapor mixture in polyethylene has also been studied to establish if selectivity occurs between various hydrocarbon types. For the binaries, the study has generally been made on one particular composition. However, on a selected system, viz., Tol-iOct, the effect of variation in composition on sorption has also been studied.

The polymer sheets (20 × 20 × 0.25 cm), as received, were washed thoroughly with acetone to dissolve any grease, etc., and then with water, followed by air drying. These were preserved in a desiccator. Small pieces of 10 mm × 10 mm were cut and used for experiments. The characteristics of the polymer used are given in Table I. The hydrocarbons used were supplied by Phillips Petroleum Co., U.S.A., with a guaranteed purity of not less than 99.5%. These were dried with molecular sieve, Linde 3A, before use.

EXPERIMENTAL

Studies on rate of sorption up to equilibrium for both pure compounds and binaries have been made on a conventional quartz spring balance having an overall repeatability of better than 2% in the lower and about 1% in the higher range of sorption.

The sorbed vapor compositions were determined in the newly designed assembly shown in Figure 1. The surge vessel (SV) above the sample chamber (SC) has a large volume to ensure that there is practically no change in the vapor

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TABLE I
Properties of Low-Density Polyethylene

Properties	Values
Density at 23°C	0.918
Melt flow index	1.97
Average mol. wt.	32,000
crystallinity, vol %	
30°C	40.6
40°C	35.0
50°C	28.7

composition, before and after sorption. The SC has been provided with a movable mercury reservoir (MR) and an amyl alcohol storage (AS).

The first phase of the experiment, till polymer–vapor sorption equilibrium is reached, is conducted in similar lines as for the spring balance. Sorption experiments are continued for about 28 h, which is generally 50 to 100% higher than equilibration time as obtained in preliminary experiments.

In the second phase, the extraction of sorbed vapor in amyl alcohol is done in the following way. MR is elevated so that the polymer sample is covered by mercury and residual vapor is pushed out into SV. The stopcock below is now closed, leaving a small quantity of mercury above it. Next, mercury is pushed into AS. A weighed quantity (about 12 g) of amyl alcohol is poured into AS which rests on mercury. MR is now carefully lowered till all the mercury and major portion of amyl alcohol enters the SC and the sample is fully immersed in alcohol. A small quantity of alcohol is left behind in the AS to ensure complete exclusion of air from the system. Extraction of sorbed hydrocarbons in alcohol, as explained above, is carried out at about 65°C overnight, which is much more than necessary.

Finally, the relative composition of the sorbed vapor is determined by analyzing the alcohol extract by gas chromatography.

Repeatability in composition has been found to be well within ±3%, which is satisfactory. Results are presented in Tables II to IV and in Figures 2 to 6.

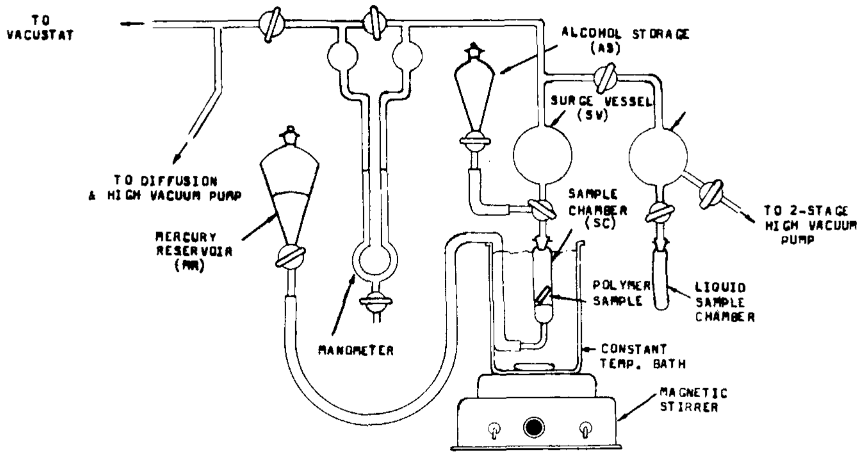

Fig. 1. Assembly for determination of sorbed vapor composition.

TABLE II
Values of Parameters for Eqs. (1) and (2)

Compounds	Temp., °C	S_0	K	$(T_R)^{-2}$
Methylcyclohexane	50	0.0162	2.6	3.13
	40	0.0194	3.8	3.35
Toluene	50	0.0191	4.7	3.39
	40	0.0200	6.1	3.60
Heptane	50	0.0112	3.6	2.79
	40	0.0128	4.1	2.97
Isooctane	50	0.0138	9.4	2.82
	40	0.0147	10.4	3.02

DISCUSSION

The polymer used for the studies has a crystallinity in the range of 40.6 vol % at 30°C to 28.7% at 50°C (Table I), the balance being amorphous. It is well known that the crystallites are impenetrable by the hydrocarbon molecules, and, consequently, sorption occurs only within the amorphous portion.

Rate of Sorption

Typical rate curves, e.g., at 30°C and 14–15 mm Hg absolute pressure, are plotted in Figure 2. All the curves show normal behavior, exhibiting a higher rate of sorption at the beginning and gradually leveling off as equilibrium is approached. Equilibrium sorption is achieved in about 20 h for some systems, indicating the rate to be slow compared to liquid sorption rates.[3] For pure compounds, both the sorption rates and equilibrium values are in the order Tol > Mch > Hep > iOct. However, the three binaries incorporating Tol reveal that the specificity owing to the difference in the molecular structures of the other constituent is insignificant, shifting all the curves to lie in a narrow range toward Tol, the most highly sorbed component. Same tendency is observed for the other binary as well.

TABLE III
Molecular Weight of Amorphous Chain Segments between Crystallites at Various Temperatures and Pressures

Compound	Temp., °C	M_c at pressure of: 14 mm	20 mm	30 mm
Methylcyclohexane	50	34	39	48
	40	38	45	50
	30	45	60	84
Toluene	50	30	35	53
	40	33	39	58
	30	47	74	—
Heptane	50	42	45	55
	40	44	50	63
	30	52	62	93
Isooctane	50	39	39	57
	40	43	43	62
	30	50	54	86

TABLE IV
Sorbed Vapor Composition and Selectivity for Binary Systems

System A B	Temp., °C	Pressure, mm Hg	Wt % vapor composition in terms of component A Residual	Sorbed	Selectivity
Tol—Hep	50	10	50.0	52.5	1.105
		11	57.5	62.6	1.273
		50	50.0	55.0	1.222
		60	50.0	57.2	1.336
		63	50.0	57.2	1.336
		64	47.1	55.1	1.378
	40	27	53.8	54.0	1.008
		50	47.5	44.0	0.862
Tol–Mch	50	22	56.2	58.6	1.103
		55	51.1	52.2	1.045
	40	24	53.5	56.2	1.115
		52	48.2	48.6	1.016
Tol–iOct	55	45	63.4	60.6	0.888
		63	60.8	62.0	1.052
	50	31	61.3	63.4	1.094
		39	57.5	59.8	1.100
Hep–iOct	55	32	64.5	67.1	1.123
		78	60.5	68.8	1.440
	50	24	68.6	71.1	1.126
		50	67.1	70.0	1.144

Equilibrium Sorption

Equilibrium sorption curves for various pure compounds and binaries as sorption vs. vapor activity p/p_0 (where p is experimental pressure and p_0 is vapor pressure at the experimental temperature, both in mm Hg) are plotted in Figures 3 and 4. In all cases, sorption increases with temperature and vapor activity, the increase being relatively slow at the initial stages and rapid subsequently. This could be satisfactorily explained by Doolittle's theory of plasticization.[4] However, in a noncrosslinked polymer like polyethylene, plasticizer action mainly consists of reducing the number of purely mechanical entanglements of the amorphous chain segments between crystallites.[5,6] In Figure 3, the curves for Mch occupy the highest position, which is thermodynamically consistent compared to Figure 2 and agrees with the results obtained[7] gas-chromatographically earlier.

In Figure 4, at 50°C all the binaries containing Tol are represented by a single curve, indicating that variation in composition of the Tol–iOct binary does not affect the sorption characteristics. Even the contributions from other accompanying molecules of widely varying structures, e.g., Mch, Hep, etc., have apparently become insignificant.

In case of condensable vapors, the sorption characteristics deviate significantly from Henry's law even at low concentrations. The vapor sorption isotherms[8–10] follow the relationship

$$S = S_0 \exp(KC) \tag{1}$$

where S is sorption of vapor, in g-mol/g polymer-mm Hg; S_0 is vapor sorption coefficient; K is constant depending upon polymer-penetrant interaction; and C is concentration of sorbed vapor, in g-mol/g polymer. The constant K has been

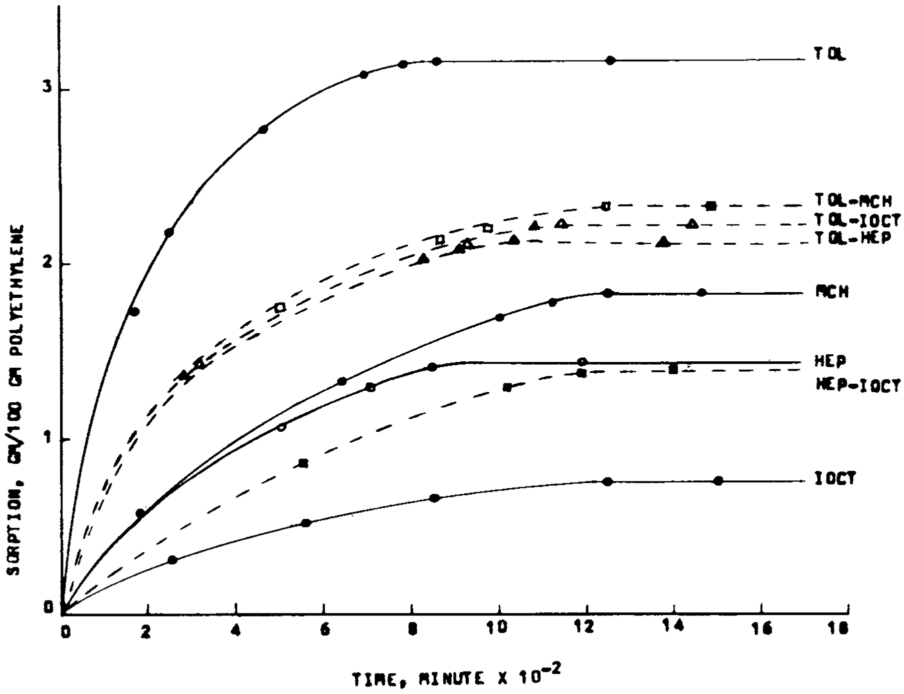

Fig. 2. Rate of vapor sorption at 30°C for pure hydrocarbon and binary.

defined to be the measure of initial sorption of unassociated penetrant into an unstrained polymer network. The polymer network is subsequently modified by stresses imposed by the sorbed molecules through plasticization as sorption proceeds. Calculated values of various parameters of eq. (1) are given in Table II.

In Figure 5, sorption at 50°C is plotted against that at 40°C for various hydrocarbons at all vapor activities. The data were converted for 100 g amorphous polymer to account for the relative change in amorphous content of the polymer at the two temperatures. The plot shows that at low sorbed concentration, plasticization is not very specific with respect to hydrocarbon types. This tendency, however, becomes prominent as the concentration increases. The relative position of the compounds in the figure generally conform to the order of values of K as obtained from eq. (1) and as such demonstrates the effect of penetrant molecular structure[11] on the degree of plasticization.

An attempt has also been made to correlate the data using the relationship[10]

$$\log S = -5.64 + 1.14(T_R)^{-2} \qquad (2)$$

where T_R is reduced temperature. This equation is claimed to be valid for various condensable hydrocarbon vapors. The values as calculated are incorporated in Table II.

Equation (2) has been graphically represented in Figure 6. The fit is generally satisfactory irrespective of experimental temperature. The slope of the curve is 0.71, comparing favorably with that of Stern et al.[10] for similar compounds.

In order to compare plasticizing effects of various hydrocarbons, the average

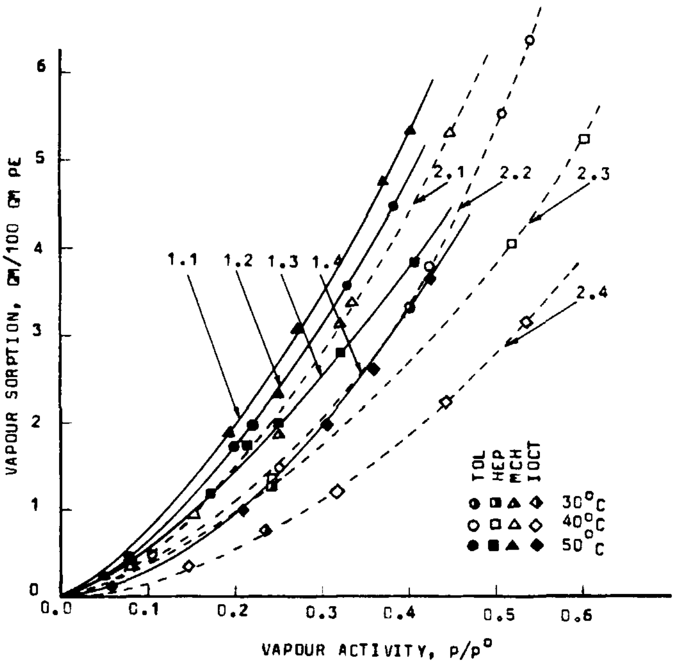

Fig. 3. Vapor activity vs. sorption of pure hydrocarbons at various temperatures. 1.1 and 2.1 Mch; 1.2 and 2.2 Tol; 1.3 and 2.3 Hep; 1.4 and 2.4 iOct. Continuous curves at 50°C; dotted curves at 30°C and 40°C.

molecular weight of an amorphous chain segment in the presence of a penetrant within the polymer network, M_c, has been calculated using the method of Baddour et al.[6] This relationship gives

$$M_c = -V_s\rho_a\left(\frac{1}{1+C^*}\right)^{1/3}\left[\ln\frac{C^*}{1+C^*}+\frac{1}{1+C^*}+X_1\left(\frac{1}{1+C^*}\right)^2\right]^{-1} \qquad (3)$$

where C^* is concn. of penetrant in purely amorphous polymer, in cm^3/cm^3; V_s is molar volume of penetrant, cm^3/mole; ρ_a is density of amorphous polymer in g/cm^3, and X_1 is the Flory–Huggins interaction parameter.

Application of the swelling theory to calculate the absolute values of amorphous chain segments by the above equation is severely restricted due to certain simplifying assumptions made and other limitations. Yet, by applying this theory, a comparison can be made among different plasticizing agents and also on the effects of concentration and temperature.

The calculated values of M_c from eq. (3) at three temperatures and three pressures are presented in Table III. The results indicate that M_c increases with vapor activity, i.e., increase in pressure and/or decrease in temperature. It is evident from the data that disentanglement of methylene chain segments occurs as the penetrant concentration increases, presumably reaching the maximum at the vapor activity of unity, i.e., in the presence of liquid. Such values of M_c have been obtained[12] in the range of 250 to 360 for these hydrocarbons from liquid sorption.

The sorption in a semicrystalline polymer like low-density polyethylene, as has been studied, is likely to depend upon two factors: (a) temperature, which

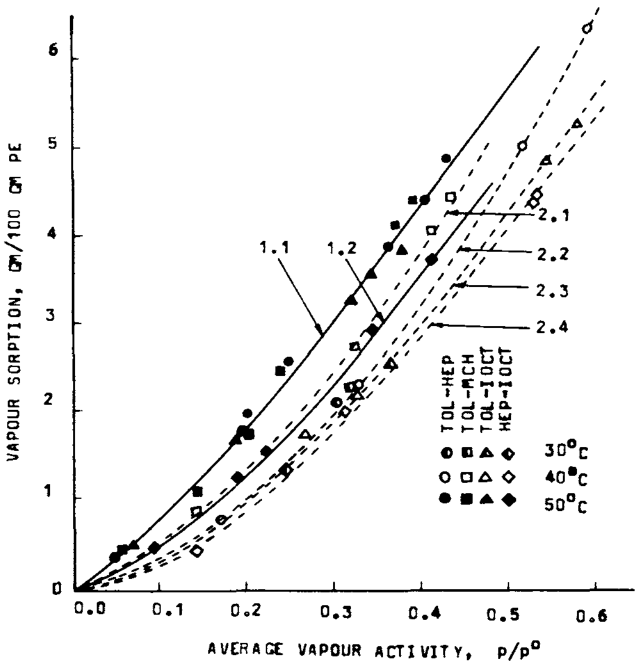

Fig. 4. Average vapor activity vs. sorption of binaries at various temperatures. 1.1 Tol–Mch; Tol–Hep, Tol–iOct; 1.2 Hep–iOct; 2.1 Tol–Mch; 2.2 Tol–Hep; 2.3 Tol–iOct; 2.4 Hep–iOct. Continuous curves at 50°C; dotted curves at 30°C and 40°C.

changes the amorphous content of the polymer and penetrant mobility; and (b) penetrant concentration, which brings about further change within the amorphous polymer chain net work. The latter is evident from Figure 5.

Selectivity in Sorption

The data on the composition of sorbed vapor within the polymer for binary mixtures are presented in Table IV. Selectivity, as reported, is defined as the ratio of the relative composition of the first component to the second in the sorbed state divided by the ratio in the residual vapor.

It is clear from the table that in all cases excepting two (viz., Tol-Hep at 40°C, 50 mm, and Tol-iOct at 55°C, 45 mm) out of 20 determinations, the selectivity is in favor of the component which is sorbed more as pure compound into the polymer. The apparent discrepancy in the Tol–Mch system is explained by the fact that at any experimental pressure, the vapor activity of Tol is considerably high compared to Mch. The results show a general trend toward the reduction in selectivity as the temperature increases and/or the pressure of vapor sorption decreases.

CONCLUSIONS

Vapor sorption in low-density polyethylene covering pure hydrocarbons and their binary mixtures was studied. At equal vapor activities, methylcyclohexane has shown maximum sorption, followed by toluene, *n*-heptane, and isooctane.

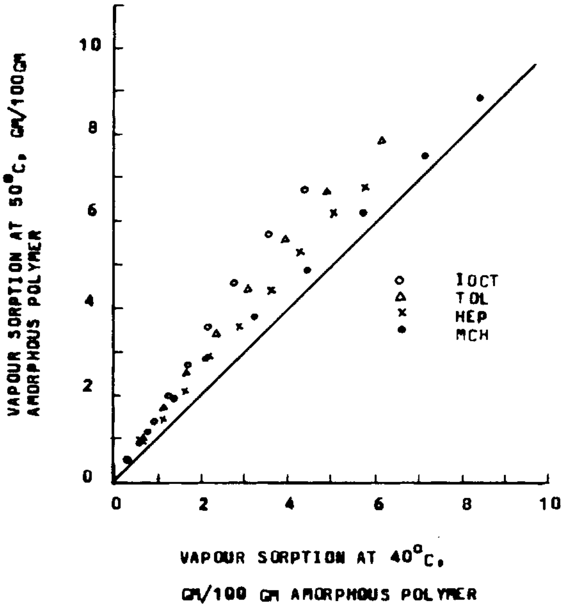

Fig. 5. Sorption of pure hydrocarbon vapor at 50°C vs. at 40°C in amorphous polymer at varying vapor activity.

The equilibrium sorption characteristics are very sensitive to temperature and pressure. The sorbed vapor composition in case of binary mixtures is dependent on feed composition.

The plasticizing effect of the penetrants has been found to be in the order iOct > Tol > Hep > Mch.

A new apparatus has been designed to generate data on selectivity of binary vapor sorption in the polymer. Results show that selectivity occurs in sorption and favors the component sorbed more as a pure compound.

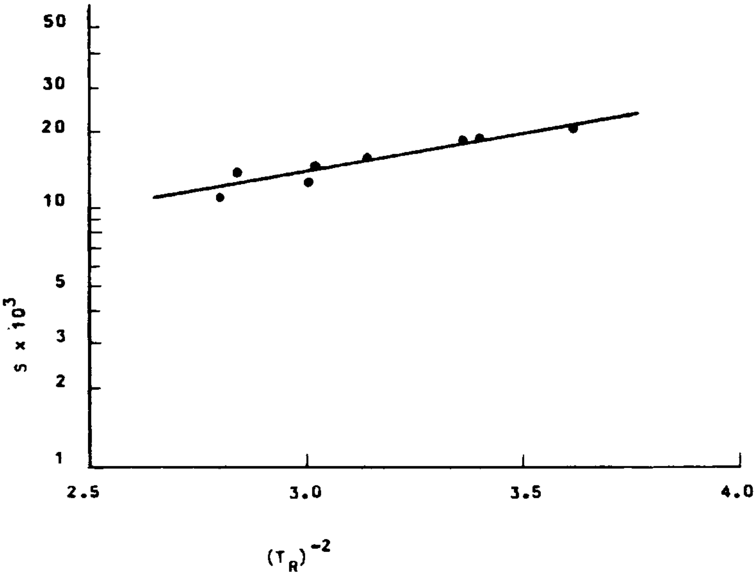

Fig. 6. Plot of log S vs. $(T_R)^{-2}$.

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