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Adsorption Equilibria of Hexane and Isopentane on Polyethylene at Different Temperatures, Pressures, and Particle Sizes

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The adsorption equilibria of gaseous hexane and isopentane on commercially available polyethylene powders were measured by a weighing method over an extensive range of temperature, pressure, and particles size. The adsorbed uptakes in adsorption equilibria were obtained at different temperatures (363.15, 358.15, 353.15, 348.15, 343.15, 338.15, 333.15 K), pressures (5.921, 9.868, 16.184, 24.736, 36.842, 53.289, 75.000 kPa), and particle sizes (0.182, 0.355, 0.566, 0.894, 1.000 mm). It was found that the uptake of hexane on polymer particles is much less than that of isopentane. An adsorption model presented by Wang et al. (*Chin. J. Chem. Eng.* **2000**, *8*, 41−45) was used to correlate the experimental data in this study with a deviation of less than 13%.

Introduction

In a gas-phase fluidized-bed ethylene polymerization process, the adsorbed uptake of volatile under different polymerization conditions must be determined clearly; this is especially true for the condensed mode technology.[1,2] The adsorbed uptake of volatiles not only affects the prediction of the devolatilization rate and holding capacity of resins in the degassing bin, but also influences the quality of fluidization because of the adsorption of volatile in fluidized particles. Hence, reliable data on adsorption equilibria are a prerequisite to the safe design of a process and the accurate prediction of the performance of the polymerization reactor and devolatilization equipment.

Although adsorption equilibrium data for monomers or comonomers in polymer particles are extensive, little information about the adsorption of higher hydrocarbons in particles was found in a search of Chemical Abstract indices. Experimental determination of adsorption equilibrium data is a new subject arising from condensed-mode polyethylene process technology, where the inert hydrocarbon is used as a condensable agent for heat removal. In this regard, the present study has been devoted to the measurement of the adsorption of hexane on polyethylene particles over a wide range of temperatures, pressures, and particles sizes. The experimental equilibrium data were further correlated satisfactorily using the adsorption model presented by Wang et al.[3]

Experimental Section

Materials. Hexane and isopentane, produced by Tokyo Kasei Chemical Industry Co. Ltd, were chosen as the adsorbates. Their purities are above 99 mass %. Refined nitrogen (>99.99 mass %) was used from Shanghai Institute of Organic Chemistry. A type of copolymer of ethylene with a low percentage of butylene as the comonomer (the ratio of butylene to ethylene is 0.08 and polymerization is by the Unipol process), obtained from Maoming Petrochemical Co. Ltd. in China, was used in our experiments. It is called linear low-density polyethylene and is commercially available in the form of resin powders, some properties of which are as follows: apparent density of particles, 0.900 g cm^{-3}; melt index, 2.0 g (10 min)$^{-1}$; actual density of particles, 0.918 g cm^{-3}; and particle diameters, 0.182×10^{-3}, 0.355×10^{-3}, 0.566×10^{-3}, 0.894×10^{-3}, and 1.000×10^{-3} m.

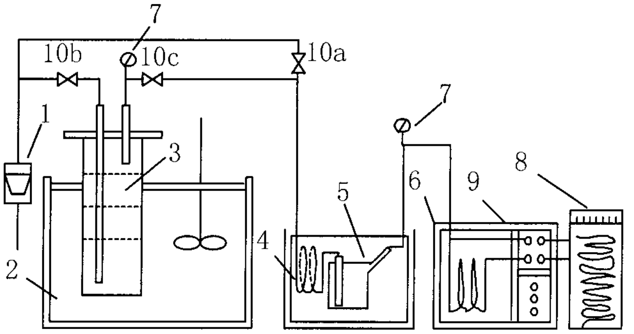

Figure 1. Experimental apparatus: 1, rotary flow meter (0−100 mL/min); 2, isothermal vessel; 3, hexane (or isopentane); 4, isothermal box; 5, adsorption bottle; 6, GC-14B chromatograph (Shimadzu); 7, manometer; 8, data display and analyzer (hydrogen flame detector); 9, chromatograph column (pipe only); 10a−c, valves.

Apparatus and Procedure. The experimental apparatus and process are shown schematically in Figure 1. A stream of pure nitrogen was passed through liquid hexane (or isopentane), which was kept at a given temperature by a controller, to produce a gas mixture with a certain concentration of hexane (or isopentane) (as the adsorbate). Then, the gas mixture was fed into an adsorption bottle that contained a known mass (typically 5 g) of polyethylene particles, and the particles in the bottle were saturated with hexane (or isopentane) after some given time. When the chromatograph detector (hydrogen flame detector) indicated that the concentration of hexane (or isopentane) leaving the bottle was constant and equal to the concentration of volatile at the inlet of the adsorption bottle (generally after 30 min), then it was assumed that the adsorption equilibrium was established. The adsorbed uptake on the polymer particles was determined from the uptake increase of the particles tested.

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Table 1. Adsorbed Uptakes of Hexane, *q*, at Different Operating Temperatures and Partial Pressures of Volatile[a]

	$q \times 10^3$ at the indicated temperatures (K)						
P_v (kPa)	333.15	338.15	343.15	348.15	353.15	358.15	363.15
5.921	3.244	2.912	2.618	2.286	1.925	1.812	1.640
9.868	3.382	3.083	2.842	2.626	2.357	2.143	1.973
16.184	3.442	3.176	2.933	2.716	2.500	2.334	2.204
24.736	3.542	3.287	3.081	2.904	2.681	2.526	2.390
36.842	3.732	3.572	3.324	3.184	2.970	2.782	2.547
53.289	3.842	3.624	3.393	3.221	3.025	2.836	2.614
75.000	3.912	3.675	3.462	3.284	3.081	2.872	2.681

[a] $d_p = 0.663$ mm.

Table 2. Adsorbed Uptakes, *q*, at Different Particle Diameters[a]

d_p (mm)	$q_{hexane} \times 10^3$	$q_{isopentane} \times 10^3$
1.000	1.481	6.365
0.894	1.886	7.388
0.566	2.407	9.025
0.355	3.132	10.958
0.182	3.594	12.400

[a] $P = 5.921$ kPa, $T = 363.15$ K.

In Figure 1, the pipe connecting the glass bottles in two isothermal vessels is artificially heated above the temperature of the isothermal vessel (2) to prevent vapor condensation. Before entering the adsorption bottle, the volatile passes a coil pipe (2 m) in the isothermal box (4) to be preheated to the desired temperature of the isothermal box (4). During the experimental run, the temperature of the isothermal vessel (2) is always lower than that of the isothermal box (4). The temperature of the isothermal vessel (2) is fixed at 0, 10, 20, 30, 40, 50, and 60 °C for the various experiments, while the temperature of the isothermal box (4) is generally 60, 65, 70, 75, 80, 85, and 90 °C, respectively. Thus, the volatile will not condense within the pipe and the adsorption bottle. Five grams of polyethylene powders can be charged to the adsorption bottle. An isothermal bath (Shanghai Instrument Co. Ltd., China) is used to control the temperature to within ±0.1 K. During an adsorption run, pressure changes were measured using a manometer (Shanghai Instrument Co. Ltd., China) with a scale of 160 kPa and an accuracy of 0.05%. In addition, the adsorbed uptake was measured by a TGA instrument (TGA/SDTA 851^e, Mettler Toledo.) to within ±0.1 μg. The ranges of operating temperature, pressure, and particle size are from 313.15 to 368.13 K, from 5 to 100 kPa, and from 0.182 to 1.000 mm, respectively.

Results and Discussion

The design of a degassing bin, the control of fluidization quality, and the capacity of heat removal in the condensed-mode process require physical data for the polymer and gaseous mixture, especially data on the adsorption equilibria for the system. For practical applications, the adsorption equilibria must be known over an extensive range of operating conditions. In addition, these data are fundamental for developing an optimization model of the condensed-mode polymerization process. In this study, the adsorption data for hexane and isopentane in polyethylene particles were measured at different operating temperatures, pressures, and particles sizes by using a weighing method. The experiment data are listed in Tables 1−3.

Table 3. Adsorbed Uptakes, *q*, at Different Operating Temperatures[a]

T (K)	$q_{hexane} \times 10^3$	$q_{isopentane} \times 10^3$
333.15	3.244	13.721
338.15	2.910	12.400
343.15	2.618	11.297
348.15	2.286	10.101
353.15	1.925	8.956
358.15	1.810	8.352

[a] $P_v = 5.921$ kPa, $d_p = 0.663$ mm.

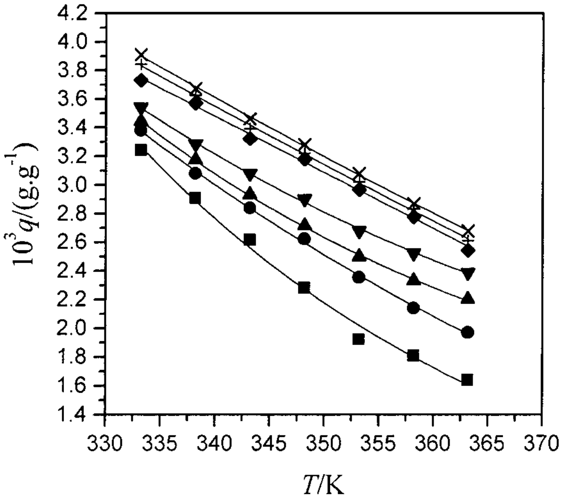

Figure 2. Adsorbed uptake of hexane in PE particles ($d_p = 0.663$ mm). Symbols: ×, 5.921 kPa; +, 9.868 kPa; ♦, 16.184 kPa; ▼, 24.736 kPa; ▲, 36.842 kPa; ●, 53.289 kPa; ■, 75.000 kPa. Curve: Wang et al.'s model.[3]

In general, the experimental data should be correlated by an analytical expression that includes some adjustable parameters as functions of temperature, pressure, and particle size. The Hery[4] model had been used by Union Carbide Corporation to calculate the adsorbed uptake of condensable hydrocarbon; however, the prediction from this model is unsatisfactory, giving deviations between the predicated data and the experimental data of up to 100%.[4] A novel model for adsorption equilibria[3] has been developed by our research group. The model is given by

$$q = \frac{q_0 d_p^I}{\sqrt{T}} \frac{B_0 \sqrt{T} \exp\left(\frac{E_d}{RT}\right) P_v}{1 + B_0 \sqrt{T} \exp\left(\frac{E_d}{RT}\right) P_v} \tag{1}$$

where q_0, I, and B_0 are model parameters; d_p is the diameter of the polymer particles; T is the operating temperature; E_d is the activation energy of adsorption; and P_v is the partial pressure of volatile. The parameters in eq 1 can be evaluated by the Gauss−Newton method under some constraints. We found that the experimental equilibrium data in this study are correlated satisfactorily by employing eq 1. The experimental data and fitting results are illustrated schematically in Figures 2−5. The average deviation between the experimental data and the results fitted by the model was found to be less than 13%. Figure 2 shows the dependence of the adsorbed uptake of volatile on the operating temperature. Figure 3 exhibits the variations of the adsorbed uptake with the volatile partial pressure. In Figures 2 and 3, the average diameter of the polymer particles is typically set at 6.63 × 10^{-4} m. Figure 4 shows the effects of particle size on the adsorbed uptake. Figure 5 shows the dependence on temperature of the uptake of hexane and isopentane. From these figures, we can summarize as follows: First, the higher the operating

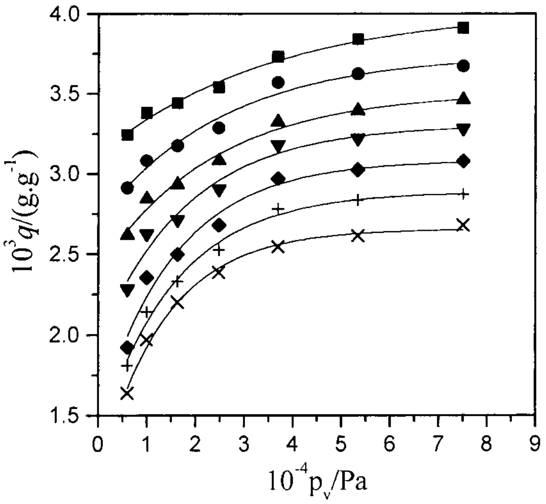

Figure 3. Adsorbed uptake of hexane in PE particles ($d_p = 0.663$ mm). Symbols: ×, 363.15 K; +, 358.15 K; ♦, 353.15 K; ▼, 348.15 K; ▲, 343.15 K; ●, 338.15 K; ■, 333.15 K. Curve: Wang et al.'s model.[3]

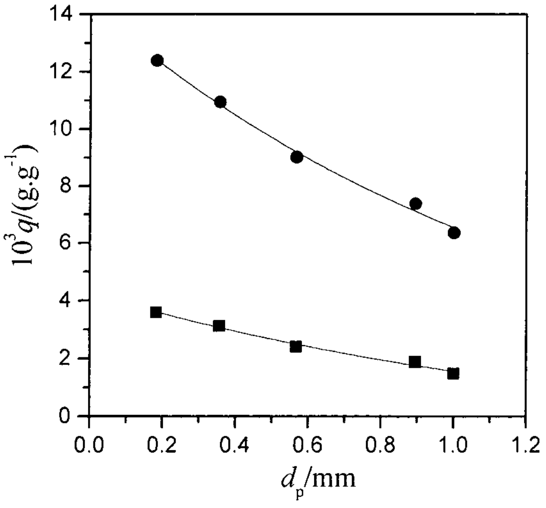

Figure 4. Adsorbed uptake of volatiles under the same operating conditions ($P_v = 5.921$ kPa, $T = 363.15$ K). Symbols: ●, isopentane; ■, hexane. Curve: Wang et al.'s model.[3]

temperature, the lower is the adsorbed uptake. The reason is evidently that the adsorption is exothermic. Second, the adsorbed uptake of volatile on particles increases with increasing partial pressure of volatile. It is well-known that an approximately linear relationship will exist if the partial pressure of volatile is not too high (generally below 10 kPa). Third, it is found that the adsorbed uptake of volatile increases with decreasing particle diameter. This can be rationalized by the corresponding increase in surface area/mass ratio. In fact, the pore structure of small particles is much more abundant, which will result in a higher polymerization activity in the reactor. Therefore, we should pay more attention to small particles. Fourth, the adsorbed uptake of hexane on particles is surprisingly much less than that of isopentane. This is an anomalous phenomenon. Generally speaking, isopentane is expected to have more difficulty entering small pores than hexane because of its branching, and the uptake of isopentane is expected to be lower. Unfortunately, however, our results are opposite to expectations. At present, our explanation is that a better ability of hydrocarbons with lower carbon numbers to penetrate and dissolve in the polymer matrix might result in higher uptakes.

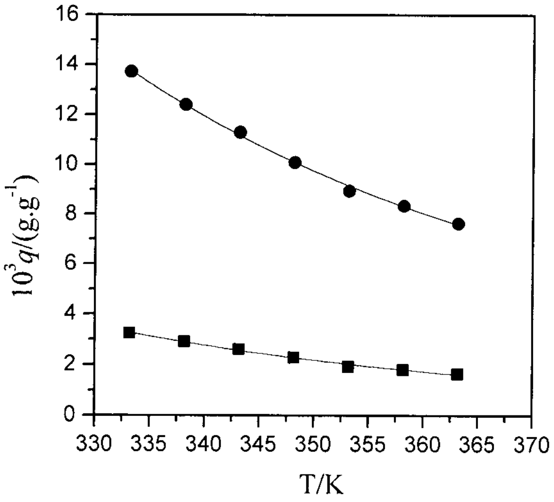

Figure 5. Adsorbed uptake of volatiles at the same partial pressure and particle diameter ($P_v = 5.921$ kPa, $d_p = 0.663$ mm). Symbols: ●, isopentane; ■, hexane. Curve: Wang et al.'s model.[3]

The subsequent results show that the model of Wang et al.[3] can provide reliable results for fitting the adsorption equilibria of volatiles on polyethylene particles. The errors are less than 13%. Moreover, the experimental method is very effective for the determination of adsorption equilibrium data.

Conclusions

New experimental data for the equilibrium adsorption of hexane and isopentane have been determined with commercially available polyethylene powders. It was found that the adsorption uptake decreases as the operating temperature increases. The adsorbed uptake of volatile increases with increasing partial pressure of volatile and decreases with increasing particle size. The adsorbed uptake of hexane on polymer powders is much less than that of isopentane. A satisfactory agreement has been obtained between the experimental data and the model presented by Wang et al.[3]

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