Determination of the Infinite Dilution Diffusion and Activity Coefficients of Alkanes in Polypropylene by Inverse Gas Chromatography

Changwei Zhao, Jiding Li, Chuyi Zeng

Department of Chemical Engineering, Tsinghua University, Beijing 100084, People's Republic of China

Received 18 August 2005; accepted 3 November 2005
DOI 10.1002/app.23658
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Infinite dilution diffusion and activity coefficients of *n*-hexane, *n*-heptane, and *n*-decane in polypropylene were measured from 373.15 to 393.15 K by inverse gas chromatography. The influences of small molecule solvent and temperature on the infinite dilution diffusion and activity coefficients were investigated. The results showed that the infinite dilution diffusion coefficient decreased but the infinite dilution activity coefficient increased with an increasing number of CH_2 group in the aliphatic solvents. The temperature increase resulted in the increase in the infinite dilution diffusion coefficient and the decrease in the infinite dilution activity coefficient. The graphs plotted according to the results of the infinite dilution diffusion coefficient versus temperature were in agreement with the Arrhenius equation. Diffusion constant and activation energy were obtained from the Arrhenius equation. Also, the interdependence on the infinite dilute activity coefficient and temperature accorded with Gibbs-Helmholtz equation. From the temperature dependence of the limiting activity coefficients partial molar excess enthalpy at infinite dilution $H^{E,\infty}$ was obtained. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1925–1930, 2006

Key words: infinite dilution diffusion coefficient; infinite dilution activity coefficient; polypropylene; inverse gas chromatography

INTRODUCTION

The molecular transport of small moleculars in polymer sheet membranes is of considerable importance in a wide variety of manufacturing operations of polymers.[1,2] Accurate measurements of the activity coefficients and diffusivities for small molecules in polymers have been a very difficult but important issue for many years. Conventional methods for measuring them rely on bulk equilibration and gravimetric sorption/desorption experiments.[3–6] These techniques, however, become very difficult to apply to the polymer–solvent systems when the solvent is present in vanishingly small amounts. Recently, the inverse gas chromatography (IGC) technique is a fast and reliable technique for measurement of the diffusion and activity coefficients at infinite dilution.[7–9]

Polypropylene (PP) has been widely used in apparel, upholstery, hygiene medical, car industry, automotive textiles, membrane preparation, wall-coverings, and so on.[10] However, there has been little experimental data reported for the infinite dilute diffusion and activity coefficient of solvent in PP. In this work, the infinite dilution diffusion and activity coefficients of *n*-hexane, *n*-heptane, and *n*-decane in PP at different temperatures were obtained by IGC. The results are beneficial to the prediction of small solvent transport in polymer and the design of membrane material.

EXPERIMENTAL

Materials

PP was purchased from Beijing Yanshan Petrochemical, People's Republic of China. *n*-Hexane, *n*-heptane, and *n*-decane were obtained as analytical reagents from Beijing Chemistry Industry, People's Republic of China.

Preparation of packed column

Chromosorb-G, whose size is of 60–80 mesh, was purchased from Shanghai first reagent manufactory of

Correspondence to: J. Li (lijiding@mail.tsinghua.edu.cn).
Contract grant sponsor: the National Natural Science Foundation of China; contract grant number: 20276034.
Contract grant sponsor: the National High Technology Research and Development Program of China (863 Program); contract grant number: 2003AA328020.
Contract grant sponsor: Postdoctoral Foundation of China; contract grant number: 023202057.
Contract grant sponsor: Major State Basic Research Development Program of China (973 Program); contract grant number: 2003CB615701.

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TABLE I
The Column Conditioning of This Experimental

Polymer	Polypropylene
Solvent	Dimethylbenzene
Carrier	102 carrier (60–80 mesh)
Mass fraction of polymer in stationary phase (wt %)	1.564
Column length (m)	1.9
Column inner diameter (mm)	3
The time of ageing (h)	10

People's Republic of China. The PP was dissolved in dimethylbenzene and coated onto the Chromosorb-G by vibrating and slow evaporation of the solvent to get a uniform polymer coating. The coated particles were then dried under vacuum to constant weight and placed in a solvent-washed 190 cm long, 3 mm i.d. stainless steel tubes, with the aid of a mechanical vibrator. The ends of the tubes were loosely plugged with steel wool. The column conditioning is listed in Table I.

IGC procedure

The gas chromatograph was SP-6800A (Shandong Lunan's Ruihong Chem. of People's Republic of China), equipped with a thermal conductivity detector. Hydrogen was used as the carrier gas in all experiments. The temperatures of the injection block and the detector were set about 50 K above the column temperature to avoid condensation in the injector and detector. Small amounts of solvent (0.4 μL) were injected in the column using a 1 μL syringe, while about 40 μL of air were injected as an inlet component along with the liquid samples to determine the average velocity of carrier gas in the column. The output from the thermal conductivity detector was fed to a chromatographic workstation for further analysis of the peaks.

The flow rate of carrier gas was measured by means of a soap bubble flowmeter. Measurements were preformed over a wide range of flow rate at each temperature. In addition, replicate experiments were done at each flow rate to ensure that the results were reproducible at each fixed set of conditions. The pressure drop across the column was measured using a highly accurate manometer at each flow rate, and then the column was set to the next flow rate.

THEORY

Diffusion coefficient

According to Van Deemter's model,[11] the infinite dilution diffusion coefficient can be obtained by the following equation:

$$D^{\infty} = \frac{8d_p^2}{\pi^2 C}\frac{k}{(1+k)^2} \tag{1}$$

where d_p is the thickness of the stationary phase and k the so called partition ratio. The thickness of the stationary phase, d_p, i.e., the polymer, is determined from the equation:

$$d_p = \frac{w_p \rho_d d_d}{6\rho_p w_d} \tag{2}$$

where w_p is the weight of the PP inside the carrier; w_d, the weight of carrier; ρ_p, the PP density; ρ_d, the carrier density; and d_d is the carrier average diameter.

The partition ratio, k, is calculated from the equation:

$$k = \frac{t_r - t_a}{t_a} \tag{3}$$

where t_r is the retention time of the solvent and t_a is the dead time required for an inert gas to pass through the column.

From Plate theory,[11] C in eq. (1) is related to column characteristics by the equation:

$$H = A + B/u + Cu \tag{4}$$

where H is the plate height equivalent to a theoretical plate; u, the mean flow rate of the carrier gas; and A, a constant related to eddy diffusion; B depends on the axial diffusion in the gas phase, and C depends on, among other things, probe diffusion in the liquid phase.

H is calculated from the experimental eluted peak as follows[12]:

$$H = \left(\frac{l}{5.54}\right)\left(\frac{d}{t_r}\right)^2 \tag{5}$$

where l is the column length and d is the measured peak width at half the maximum height.

The linear velocity of the carrier gas, u, is calculated from the expression:

$$u = \frac{jF}{a}\frac{T_{\text{col}}}{T_{\text{fm}}} \tag{6}$$

where j is the compressibility factor determined from

$$j = \frac{3}{2}\frac{\left[\left(\frac{P_{\text{in}}}{P_{\text{out}}}\right)^2 - 1\right]}{\left[\left(\frac{P_{\text{in}}}{P_{\text{out}}}\right)^3 - 1\right]} \tag{7}$$

where P_{in} and P_{out} are the inlet and outlet pressures of the column, respectively. Therefore, at each temperature and velocity of carrier gas, the compressibility factor can be determined directly from the measured data of P_{in} and P_{out}. T_{col} and T_{fm} are the temperature of the column and flow meter, respectively; $\bar{a}$ is the volume of gas phase per unit length and is determined by dividing the retention volume of air by the column length; and F is the carrier gas volume flow.

These results may be used to determine diffusivity from experimental data as follows: solute elution curves are obtained for a range of flow rates. From measurements of peak width, a plot of H versus u is prepared. At sufficiently high flow rates, the term B/u is small in relation to $A + Cu$, and the second term on the right-hand side of eq. (4) becomes negligible and the plot of H versus u should yield a straight line with a slope C. If the partition ratio k and the film thickness d_p are determined, the infinite dilution diffusion coefficient of solvent in polymer D^{∞} can be obtained from C with eq. (1).

Activity coefficient

The generalized equations relating the measured data to activity coefficients of solvent in polymer were given as follows:

$$\gamma_1^{\infty} = \frac{273.15R}{v_g^0 M_2} \frac{1}{\varphi_1^s P_1^s} \quad (8)$$

$$v_g^0 = \frac{F}{\omega 2} \frac{P_{fm} - P_w^s}{760} \frac{273.15}{T_{fm}} \frac{3}{2} \frac{(P_{in}/P_{out})^2 - 1}{(P_{in}/P_{out})^3) - 1} \times (t_r - t_a) \quad (9)$$

where R was the gas constant, M_2 the molar mass of polymer, w_2 the mass of polymer on the inert carrier material packed in the column, t_r the retention time of the solvent, t_a the dead time required for an inert gas to pass through the column, F the carrier gas volume flow measured by the soap bubble flowmeter at the pressure, P_{fm} and temperature, T_{fm}, P_w^s the saturated vapor pressure of water at T_{fm}, P_{in} and P_{out} were the column inlet and outlet pressure, respectively, and P_1^s was the saturated vapor pressure of the pure solvent. The saturated vapor pressures of solvents were calculated by use of Antoine constants taken from the Dortmund Data Bank (DDB). The saturated fugacity coefficients of the solvents φ_1^s were calculated according to the Soave equation of state; the necessary critical properties and acentric factors were also taken from DDB.

RESULTS AND DISCUSSION

The IGC was used to measure the infinite dilution diffusion and activity coefficients of *n*-hexane, *n*-heptane, and *n*-decane in PP at different temperatures. Measurements for each solvent–polymer pair were obtained at several carrier flow rates. To test the applicability of the van Deemter equation, plots of plate height, H, versus linear velocity, u, were constructed for each solvent in PP at different temperatures. Figure 1 illustrates the linear relationships of H with u for solvents (*n*-hexane, *n*-heptane, and *n*-decane) in PP

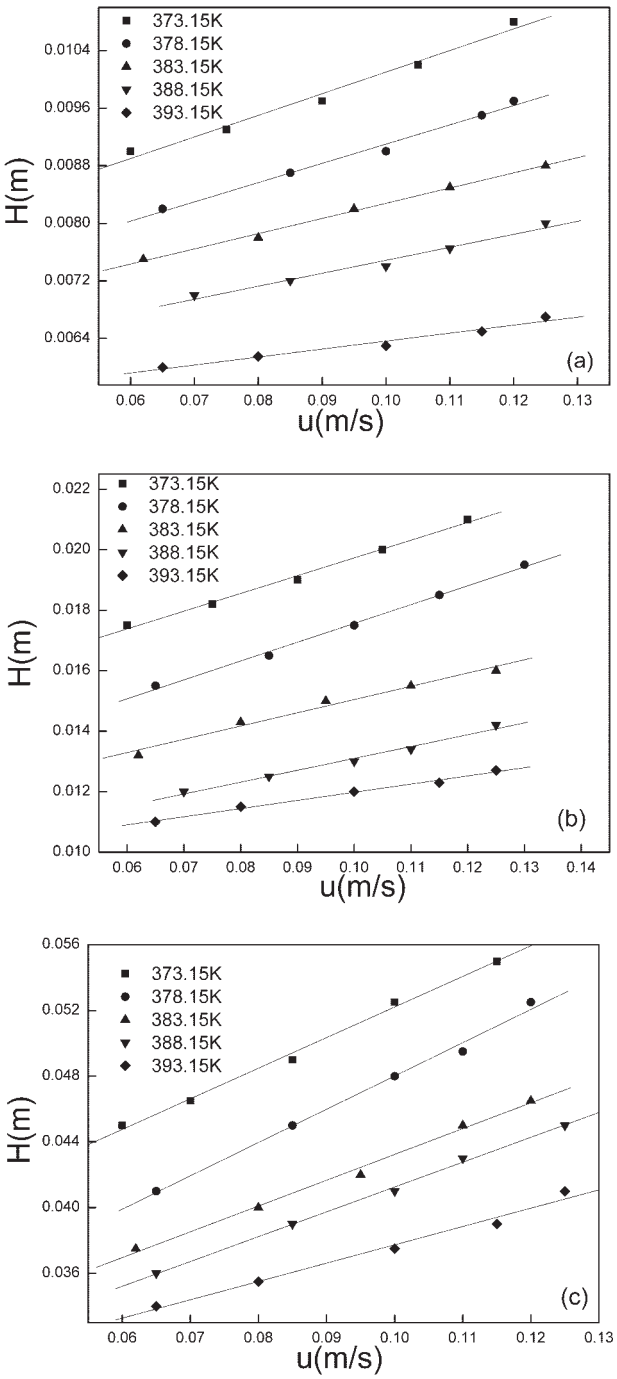

Figure 1 Relationship between the flow rate and the plate height of different solvents in PP at various temperatures. (a) *n*-hexane; (b) *n*-heptane; (c) *n*-decane.

TABLE II
The Infinite Dilution Diffusion Coefficients of Small Molecule Solvents in Polyproylene at Various Temperatures

	$D^{\infty} \times 10^{11}$ (m^2/s)		
T (K)	*n*-Hexane	*n*-Heptane	*n*-Decane
373.15	1.667	0.832	0.258
378.15	2.464	1.276	0.336
383.15	3.287	1.996	0.441
388.15	4.025	2.657	0.534
393.15	4.986	3.263	0.628

from 373.15 to 393.15 K. The values of the C at each temperature were determined from the slope of the lines. These values were then used in eq. (1) to estimate the diffusion coefficient in polymer phase, D^{∞}, and the values of the appropriate diffusion coefficients are listed in Table II. Equations (8) and (9) were used to estimate the activity coefficient, and the infinite dilution activity coefficients are listed in Table III.

From an examination of the data listed in Table II it was clear that the infinite dilution diffusion coefficient of the aliphatic solvents, *n*-hexane, *n*-heptane, and *n*-decane in PP at the same temperature decreased in the order:

$$n\text{-hexane} > n\text{-heptane} > n\text{-decane}$$

This difference may be related to a number of factors such as size and shape of the solvent molecule, the size of the hole required to accommodate the molecule. The effect of the size of the molecules of these solvents may be investigated through knowledge of their molar volumes, which have the order:

$$n\text{-decane} > n\text{-heptane} > n\text{-hexane}$$

During diffusion the length and the size of the path the molecule must follow the free volume available to the polymer segment to exchange positions with the solvent molecules. The bigger solvent molecule was disadvantageous to diffuse in polymer. To describe the influence of the solvent molecule on diffusion coefficient, a plot of logarithm D^{∞} against solvent molecular weight are shown in Figure 2. From Figure 2, it can be seen that the logarithm of the diffusion coefficients showed inverse proportionality to the size of the solvent molecular. This result agreed well with Einstein's equation for the diffusion coefficient relating to the chain length of the solvent which had the form:[13]

$$D^{\infty} = \frac{KT}{\pi r_A \eta_B} \tag{10}$$

where K is the Boltzmann constant, T is absolute temperature, and r_A is the radius of the molecule and directly proportional to the chain length.

From Table II it can be seen that the temperature played a very important role on the diffusion process. In general, the temperature dependence of the diffusion coefficient is given by Arrhenius equation:

$$D = D0e^{-\Delta ED/RT} \tag{11}$$

where D_0 is the pre-exponential factor of the diffusion process independent from the temperature and ΔE_D is the activation energy for a diffusant compound in a given polymer matrix to escape from its present surroundings and move into an adjacent different surrounding. R is the gas constant, and T is absolute temperature. In dilute solutions, where the diffusing species does not often encounter a polymer molecule, the diffusion rate is limited by the energy required for the diffusing species to escape its present surroundings and move into an adjacent environment. Figure 3 indicates that the plot of versus In D^{∞} $1/T$ is linear which confirms that ΔE_D is independent of temperature in the covered range. The activation energies for three penetrants were calculated from the fitted

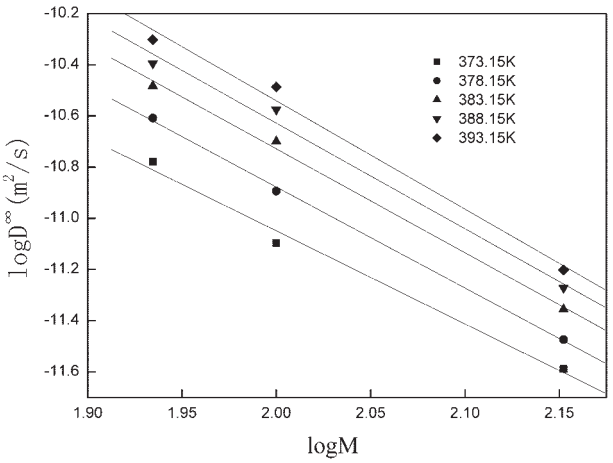

Figure 2 Relationship between the infinite dilution diffusion coefficient and molecular weight of aliphatic solvents in PP at various temperatures.

TABLE III
The Infinite Dilution Activity Coefficients of Small Molecule Solvents in Polyproylene at Various Temperatures

	γ^{∞}		
T (K)	*n*-Hexane	*n*-Heptane	*n*-Decane
373.15	0.665	1.427	4.952
378.15	0.616	1.298	4.483
383.15	0.558	1.142	4.082
388.15	0.512	1.023	3.669
393.15	0.455	0.886	3.394

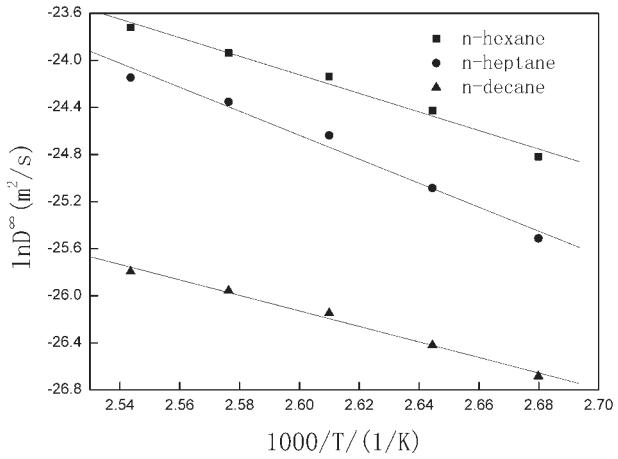

Figure 3 Relationship between the infinite dilution diffusion coefficient and temperatures in PP.

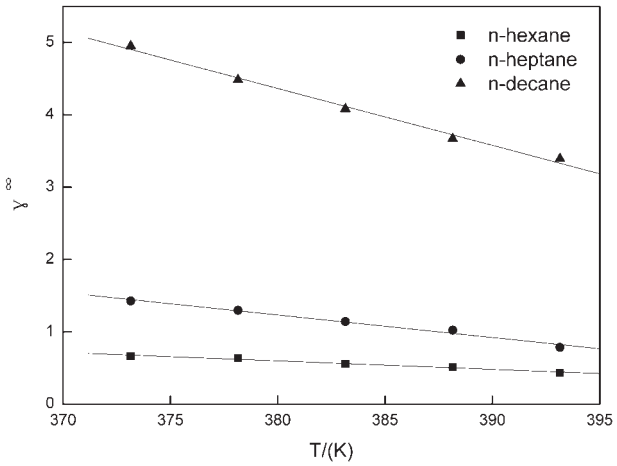

Figure 4 Relationship between the infinite dilution activity coefficient and temperature in PP.

straight lines and shown in Table IV. As shown in Table IV, diffusion activation energy was positive, that is to say the process of solvent molecule diffusion in polymer was endothermic. The longer chain of solvent molecule caused a decrease of activation energy. The same consideration can explain the deviation for the diffusion constant.

As shown in Table III, the γ^{∞} of solvents in PP displays an increase as the number of carbon atoms in the molecules increases at each temperature. The reason may be that the longer the alkane chain is, the larger of the alkane molecular volume is. The larger solvent molecule was disadvantageous to dissolve in polymer, which resulted in the increase of infinite dilution activity coefficient of alkane molecular in PP. The infinite dilution activity coefficient of solvent in PP decreases with the increase in temperature. The temperature dependence of the activity coefficients is presented in Figure 4. In this work, the following simple expression is proposed to give an approximate representation of the relation between γ^{∞} and temperature:

$$\mathrm{In}(\gamma^{\infty}) = a + b\,[1/(T/K)] \tag{12}$$

where a and b are solvent-dependent parameters which can be correlated with the connectivity indices of the solvent. The coefficients a and b, the correlation coefficients R^2 are given in Table V. The quality of the linear regression is good since the correlation coefficients lie above 0.99.

According to the Gibbs-Helmholtz equation, the value of the partial molar excess enthalpy at infinite dilution $H^{E,\infty}$ can be directly obtained from the slope of a straight line derived from equation:

$$\left(\frac{\partial \mathrm{In}\gamma_i^{\infty}}{\partial(1/T)}\right)_p = \frac{H_i^{E,\infty}}{R} \tag{13}$$

where R is the gas constant. The correlated $H^{E,\infty}$ values for the systems discussed in this work are also listed in Table V. As shown in Table V the values of $H^{E,\infty}$ are positive and increase with increasing chain length of the linear alkanes in PP.

CONCLUSIONS

In the present investigation, the infinite dilution diffusion and activity coefficients of *n*-hexane, *n*-heptane, and *n*-decane in PP were determined at several different temperatures by IGC. The experimental data showed the following relationships of the diffusion and activity coefficients with temperature and molecular size of solvent. Firstly, for a certain small molecule solvent, the infinite dilution diffusion coefficient increased but the infinite dilution activity coefficient

TABLE IV
The Diffusion Activation Energy and Diffusion Constant of Solvents in PP

	n-Hexane	*n*-Heptane	*n*-Decane
D_0 (m^2/s)	3.413	3.427×10^{-1}	8.271×10^{-4}
ΔE_D (KJ/mol)	80.75	75.34	60.73

TABLE V
Coefficients of eq. (12), Correlation Coefficient R^2, and Values of $H^{E,\infty}$ Derived from eq. (13) of Solvents in Polypropylene

Solvents	*a*	*b*	R^2	$H^{E,\infty}$ (KJ/mol)
n-Hexane	−7.8092	2766.4	0.9928	17.67
n-Heptane	−8.9865	3491.9	0.9937	21.88
n-Decane	−2.5039	1532.1	0.9934	22.98

decreased with the temperature increase. Second, at the same temperature, the infinite dilution diffusion coefficient decreased in the order of *n*-hexane, *n*-heptane, and *n*-decane, which were the inverse trend in the infinite dilution activity coefficient. The observed solvent diffusivity data for solvent/PP systems were also correlated using Arrhenius equation, and diffusion constant and activation energy were obtained. Meanwhile, from Gibbs-Helmholtz equation the limiting activity coefficients partial molar excess enthalpy at infinite dilution $H^{E,\infty}$ was also obtained.

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