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Measurement of Activities of Toluene and Trichloroethylene in Polyisobutylene

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Activities of trichloroethylene in polyisobutylene and toluene in polyisobutylene were measured at 23.6 °C. The corresponding polymer−solvent interaction parameters were also calculated.

Introduction

To our knowledge, the activity data of low concentrations of trichloroethylene in polyisobutylene (PIB) are not available in the published literature. Such data are useful in evaluating and modeling the performance of some types of sensors that produce a signal by chemisorption of an analyte into a polymer.[1,2] An isothermal experiment was conducted to measure the activity of trichloroethylene in a PIB−trichloroethylene solution. The activity of toluene in PIB was also measured to validate the experimental apparatus and procedure, and those data were consistent with previously published data.[3]

Experimental Section

Materials. The polymer studied in the work was polyisobutylene (PIB: #040A, viscosity average MW 400 000, Tg = −73 °C, $\rho = 0.92$ g·cm^{-3}, Scientific Polymer Products, Ontario, NY). The solvents were toluene (purity 99.8 %, Fisher Scientific, Fair Lawn, NJ) and trichloroethylene (purity 99.9 %, Mallinckrodt Chemical, Paris, KY). The two solvents were degassed to remove air and any other dissolved light contaminants by boiling off and discarding more than 10 % of the chemical. PIB films were made by dissolving PIB in trichloroethylene and casting this solution onto clean glass Petri dishes. The solvent was evaporated at room temperature, and then the film was vacuum-dried for several hours. The polymer films, which were about 0.1 mm thick, were carefully removed from the Petri dishes and placed in cups made from copper mesh. The polymer films were vacuum-dried and weighed immediately before the sorption measurements.

Experimental Apparatus. An isothermal swelling experiment was performed using the apparatus schematized in Figure 1. The total pressure of the polymer and solvent system was measured at various concentrations of the solvents in the polymer. Measurements were made only at low vapor pressures of the solvents. To ensure that no solvent vapor condensed in the tubing, the maximum vapor pressure was less than 70 % of the saturation pressure at the local room temperature of 22.5 °C to 24 °C. The glass cell was made of thick-walled Pyrex with a Teflon cap. The cap screws into the cell and forms a seal with a Viton O-ring. Some vacuum grease was placed on the external side of the O-ring/glass/Teflon junction. The 1.6 mm steel tubing connected through the cap provides for the addition of solvent components and for vacuum degassing. To monitor the vapor temperature in the cell, a platinum resistance thermometer was inserted into a thermowell, which extends into the cell. The same type of platinum thermometer was also used to monitor the temperature of the water bath. The change of resistance of the platinum thermometer was read from a digital scanner (model 199 System DMM Scanner, Keithley Instrument, Cleveland, OH).

The desired quantity of toluene or trichloroethylene was charged to the evacuated cell using a weighed syringe. The amount of trichloroethylene or toluene injected into the cell was calculated more precisely by reading the initial change of the cell pressure than by measuring the syringe mass because some liquid was trapped outside of the charging valve. The cell pressure was measured with a digital vacuum gauge (Digital Test Gauge 2089, Ashcroft, Stratford, CT). The vacuum gauge monitors the relative pressure (gauge) in the range 0 Pa to 10^5 Pa and has a resolution of 7 Pa. Atmospheric pressure was measured with a mercury barometer located adjacent to the experimental apparatus. The pressure data read from the mercury barometer were corrected for temperature and elevation. The actual vapor pressure in the cell was obtained by adding the pressure obtained from the digital vacuum gauge to the barometric pressure. The uncertainties of the vapor pressure value were estimated to be within ± 14 Pa.

The platinum thermometers were calibrated using ice and steam points. Their accuracy in this apparatus was estimated to be ± 0.1 K. During the course of a measurement, the temperature of the vapor in the cell shown on the scanner was at 23.6 ± 0.1 °C. The temperature of the water bath was controlled by a precision temperature controller (Bayley Instrument, Kenwood, CA) at 23.6 ± 0.1 °C.

The total volume that the solvent vapors occupied includes two parts: the volume of the glass cell, which is under the water, and the internal volume of the tubing and valves, which are above the water. The volume of the glass cell, whose temperature was controlled precisely around 23.6 °C by the water bath, has a volume of 270.9 cm^3. This volume was measured by filling the cell with water and weighing the cell. The total volume including the glass cell, tubing, and valves was determined by measuring the pressure change following each of several 5 mL injections of air into the cell. By applying the ideal gas equation of state, the average total volume was calculated as 291.9 ± 2.1 cm^3.

Thus the internal volume of the tubing and valves, whose temperature was consistent with the air chamber and between 22.5 °C and 24.0 °C, is 21.0 cm^3. This volume is 7.2 % of the total volume. When the copper mesh and the PIB film were placed into the glass cell, their volume reduced the total volume by 0.9 cm^3.

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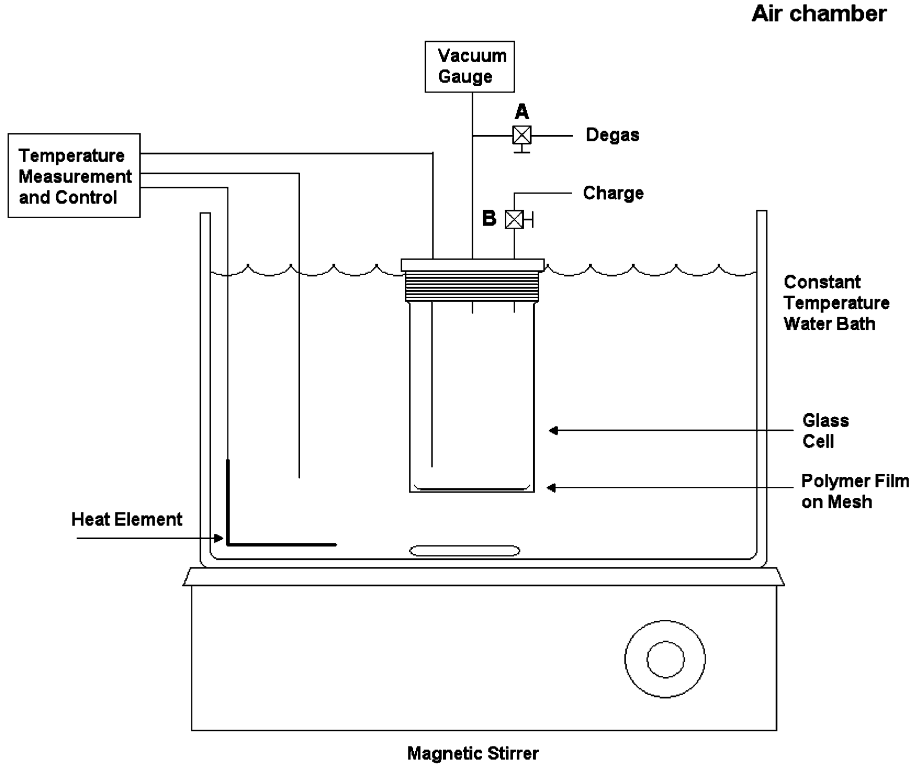

Figure 1. Vapor pressure apparatus.

Experimental Procedure. Because the rubber O-ring has similar properties as PIB and can absorb the solvents and the internal surface of glass and tubing may also adsorb some solvent, their absorption or adsorption was calibrated before the absorption of solvents by PIB films were measured. The calibration used the same procedure as the measurement of absorption into PIB, which was as follows.

Before each measurement, the whole system was evacuated to be less than 20 Pa for 48 h. Then the cell was charged with an amount of one solvent by a glass syringe with a luer lock fitting. The initial pressure change indicated the amount of mass injected, as mentioned previously. Equilibrium was assumed when no change of pressure was observed within 6 h. At equilibrium, the time, temperature, and the pressure shown on the digital gauge and the barometer were recorded. The pressure data of the barometer were corrected for the temperature dependence of the density of mercury and for the vapor pressure of mercury. To ensure that no solvent vapor condensed in the tubing, the maximum vapor pressure was always less than 70 % of the saturated pressure. At these low pressures, no liquid was ever observed inside the glass chamber.

To evaluate the experimental method, apparatus, and procedure, the absorption of toluene vapor into PIB was measured first. The results were compared with published data.[3] After a satisfactory comparison with the published data, measurements of trichloroethylene vapor absorption in PIB were performed.

Data Reduction. The amount of solvent vapor absorbed by the PIB film was obtained by measuring the change in system pressure between the initial pressure following injection and the equilibrium. This pressure change was converted to the mass of solvents by applying the ideal gas equation. The mass fractions of solvents in the swollen polymer composites were then calculated. The activities were calculated based on eq 1

$$a_1 = \frac{P}{P_1^{\mathrm{sat}}} \tag{1}$$

Table 1. Properties of Compounds at 23.6 °C[a]

	polyisobutylene	toluene	trichloroethylene
P_{sat}/Pa	n/a	3490	9082
ρ/(g·cm^{-3})	0.92	0.865	1.460
M/(g·mol)	400 000	92.138	131.388

[a] The data for trichloroethylene and toluene are from the DIPPR database.[5] The data for polyisobutylene are from the manufacturer.

Table 2. Activities of Toluene (1) in PIB (2) at 23.6 °C

w_1[a]	a_1
0.0095	0.0791
0.0105	0.1252
0.0183	0.1373
0.0243	0.1801
0.0256	0.2460

[a] w_1 is the mass fraction of solvent in polyisobutylene.

where a_1 is the activity, and P and P_1^{sat} are actual pressure and saturated pressure of the analyte, respectively. All properties applied in the calculation are listed in Table 1. At the very low vapor pressures of these experiments, corrections for the nonidealities of the solvents were on the order of only 0.067 % and were neglected in further calculations.

Results

The PIB + toluene binary system was used to evaluate the experimental method and apparatus. Only activities at low vapor concentrations were measured. The results were compared with the published data[3] as shown in Table 2 and Figure 2. A UNIQUAC model of the PIB + toluene binary system was derived based on the published data.[3] Figure 2 shows that our experimental data points are very close to the UNIQUAC model and appear to be consistent with published data, which were measured at higher vapor pressure than used herein. This indicates that our experimental data are consistent with the published data and that our experimental method and apparatus appear to be good.

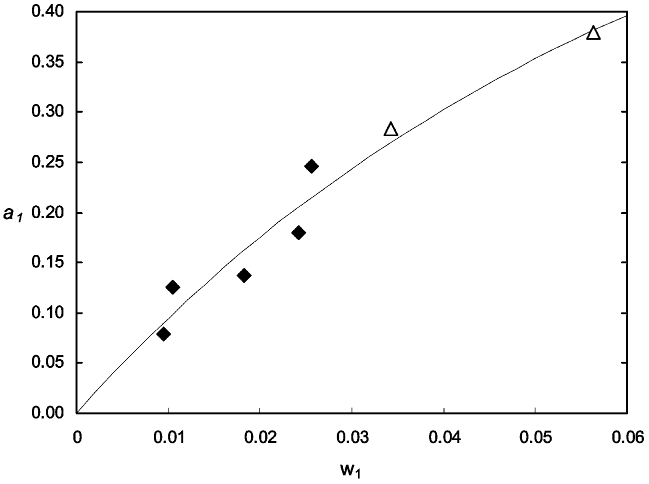

Figure 2. Activity of toluene a_1 vs its mass fraction w_1 at 23.6 °C in PIB + toluene system. △, published data;[3] —, UNIQUAC model correlated with the published data;[3] ♦, experimental data in this work.

Table 3. Activities and Interaction Parameters of Trichloroethylene (1) in PIB (2) at 23.6 °C

w_1	a_1	ϕ_1[a]	χ[b]	χ[c]
0.0047	0.0267	0.0030	1.209	0.951
0.0102	0.0499	0.0065	1.061	0.960
0.0177	0.0760	0.0113	0.943	0.971
0.0244	0.1006	0.0155	0.915	0.981
0.0274	0.1253	0.0175	1.024	0.986

[a] ϕ_1 is the volume fraction of solvent in polymer solution. [b] χ is the interaction parameter calculated from each experiment. [c] χ is the interaction parameter calculated from a regressed linear model.

The activity data and Flory−Huggins interaction parameters of the PIB + trichloroethylene binary system in this work are shown in Table 3 and Figure 3. We can see that the activity data in the range of low vapor pressure can be fitted by a linear model. There are no previously published experimental data to compare.

Discussion

General Observations. In this work, the activities of toluene and trichloroethylene in PIB were estimated using an apparatus measuring equilibrium vapor pressure. These measurements are unique in that they were done using very low pressures of the solvents. The activity of toluene in the toluene and PIB systems has been reported previously but never at pressures as low as those reported herein. Figure 2 shows that the measured activity of the toluene is consistent with the values reported at higher pressures. The new data are also consistent with predictions using UNIQUAC.

In Figure 3, the activities of trichloroethylene in PIB measured in this work were compared with activities derived from the group contribution model UNIFAC-FV.[4] It is shown that the activities measured in this work significantly deviate from the activity data estimated from UNIFAC-FV. Although UNIFAC-FV can be applied for many types of polymers and solvents, it was not recommended for systems of alkane polymers and chlorinated solvents.[4] Thus, it is not surprising that our experimental data do not agree with predictions from the UNIFAC-FV model.

The values for a_1 and χ shown in Table 3 are calculated from the experimental values of the corresponding mass and volume fractions. Thus, these values contain errors from the errors in accuracy and precision inherent in the experiment. Reason dictates that the values of χ should not jump from 1.21 to 0.92 and then back to 1.02 as ϕ_1 increases monotonically but should be fairly constant. In fact, the interaction parameter is not strictly constant even at low-solvent vapor pressures. It increases slowly along with the increase in activity or in volume fraction of the trichloroethylene, but it should not be very sensitive to the activity at low vapor pressure. The values of χ can be fit to a linear model to smooth out the data, resulting in a regression model of $\chi = 2.387\phi_1 + 0.944$ when $0 < \phi_1 < 0.02$. These values are presented in Table 3. One could also simply average the χ values over this range to obtain a mean value of 0.97. Although this value might appear high for a polymer−solvent interaction, for many polymer−solvent pairs the interaction parameters of the solvents increase as the polymer fraction increases and decrease as temperature increases. The interaction parameters in Table 3 were obtained at 23.6 °C and very high PIB concentrations (> 98 %), so it is not surprising that these values are fairly high.

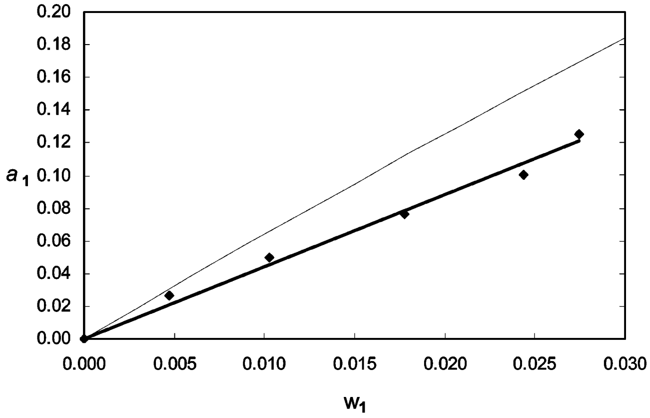

Figure 3. Activity of trichloroethylene a_1 vs its mass fraction w_1 at 23.6 °C in PIB + trichloroethylene system. —, data derived from UNIFAC-FV group contribution model;[4] ♦, experimental data in this work; —, linear fit to the experimental data.

The activity values in Table 3 also contain noise; a linear regression of the activity data in Table 3 results in the model $a_1 = 4.4034\ w_1$, as shown in Figure 3.

Potential Sources of Error. The total volume of this experimental system involves two parts, as explained previously. The temperature of the glass cell was controlled at 23.6 °C, while the tubing temperature was in the range of 22.5 °C to 24.0 °C. During the experiments, we tried to maintain the tubing temperature to be no higher than 23.5 °C by enclosing the apparatus in a framework of plastic sheeting and controlling the temperature therein and the room temperature of the lab. Otherwise, the water bath could not be controlled with precision at 23.6 °C. Any excursions of the tubing temperature higher than 23.5 °C were very short. Therefore, in the worse case the tubing temperature was 1.1 °C lower than the temperature of the glass cell. Because the volume of the tubing is only 7.2 % of the total volume, the 1.1 °C lower tubing temperature may generate −0.027 % error to the system pressure. Obviously, this error is negligibly small.

The glass cell was sealed with an O-ring and high vacuum grease. Although application of vacuum grease helped greatly, air could still diffuse into the system very slowly. This diffusion rate appeared to be constant because the system pressure always remained very low and increased fairly linearly with time. The final absorption data were obtained by subtracting this “calibration data” (which also accounted for the absorption in the O-ring and adsorption on the glass and tubing) from the total absorption measurement.

The error in the barometer reading is estimated at ± 14 Pa. When the vapor pressure is low, such as 680 Pa, this would produce about 2 % error. This error decreases as the vapor pressure increases. There is also error in the measurement of the amount of injected solvent. This error is less than 1 % for the PIB−trichloroethylene system and about 1.5 % for the PIB + toluene system. Therefore, in the worst case, the total error is estimated to be about ± 3 % for the PIB + trichloroethylene system and ± 3.5 % for the PIB + toluene system. The error in accuracy of only 3.5 % for this latter system is supported by the data shown in Figure 2, which despite some scatter from error in precision, matches fairly accurately with previous data and the fit of that data to the UNIQUAC equations. Applying the estimate of 3 % for the PIB−trichloroethylene system, the data shown in Figure 3 indicates that the UNIFAC-FV equations are not able to accurately represent this system at low-solvent volume fractions.

Conclusions

The activities and interaction parameters of trichloroethylene in polyisobutylene at 23.6 °C were obtained successfully by measuring the absorption of PIB in trichloroethylene vapor. To evaluate the measurement method, the same equipment and calculation method were used to measure activities of toluene in PIB. The results showed that the activities of the PIB−toluene system we measured were consistent with the published data.

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