Solubility and Sorption Energetics of Methyl Salicylate in Chloro-Butyl Rubber

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ABSTRACT: Equilibrium solubilities of methyl salicylate (MS) in chloro-butyl rubber (CIIR) are measured at 318 and 333 K at several MS vapor pressures. The partial molar enthalpy of absorption, H_{abs}, of MS(g) in CIIR and the partial molar enthalpy of mixing, H_{mix}, of MS(l) in CIIR are derived from the measured isotherms. The enthalpies are regarded as constant in the present concentration interval, and H_{abs} and H_{mix} are -50.3 ± 3 kJ (mol MS(g))$^{-1}$ and 4.7 ± 3 kJ (mol MS(l))$^{-1}$, respectively. The Flory interaction parameter is calculated from the enthalpy of mixing, and the obtained Flory solution model agrees well with the present solubility data. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3300–3303, 2008

Key words: barrier; rubber; thermodynamics

INTRODUCTION

Chloro-butyl rubber (CIIR) is a barrier material that is chemical-resistant and has low permeability of gases, vapors, and organic liquids.[1,2] CIIR is used in chemical protective clothing in industry, medicine, agriculture, and military. In military applications, protection must be provided against the threats of chemical warfare agents (CWA) and toxic industrial chemicals. To investigate barrier properties against these hazardous chemicals, experiments are often performed using less toxic model compounds or simulants of the real agents. Methyl salicylate [O-hydroxybenzoic acid methyl ester (MS)] is often used to simulate evaporation of liquid sulfur mustard [bis(2-chloroethyl) sulfide (HD)], which is a CWA with similar vapor pressure[3,4] as MS. However, the ability of MS to simulate sorption of HD into CIIR needs to be investigated, since the molecular structure of MS does not resemble the structure of HD. The amount of MS or HD that is absorbed into CIIR depends on both the energetics and the kinetics of the process. This work reports the equilibrium solubility and the sorption energetics of MS in CIIR at 318 and 333 K. These relatively high temperatures were chosen to investigate the barrier properties of CIIR in a hot climate.

The solubility and sorption energetics of HD in CIIR have not been reported elsewhere. The literature only describes the measurements of the solubility, diffusivity, or breakthrough times of HD in butyl rubber (IIR)[5–8] and other polymer materials.[6–11] IIR and CIIR are chemically related, but the solubility of HD in IIR has only been reported at 298 K at a single vapor pressure.[5–8] Hence, measurements of HD in CIIR should be compared with the results obtained to decide if MS satisfactorily simulates the sorption of HD.

EXPERIMENTAL

The CIIR barrier material (density, 1.18 g cm^{-3}) was supplied by Avon Protection (Melksham, UK), and MS (>99%) was purchased from Sigma Chemical (St. Louis, MO). A microtome (Microm HM 355 S) was used to cut CIIR into 0.1-mm slices to provide thin samples.

Figure 1 shows the simple glass set-up that measured the solubility of MS in CIIR at different temperatures and MS(g) vapor pressures. The two test tubes (a and b) contained the polymer sample and the liquid MS, respectively. Tubes (a) and (b) were kept at different temperatures using two separate water baths, and the glass bridge between the tubes was heated to avoid condensation. The MS vapor pressure[3] above the sample was determined by the temperature of tube (b), and the sample was taken out of tube (a) and weighed using a microbalance (Mettler Toledo MT5, Virollay, France) to measure the amount of MS absorbed into CIIR.

The samples were preheated at the experimental temperatures to desorb water and plasticizers, and the weight of the samples was almost stable prior to the MS(g) exposure. Thus, the weight change during

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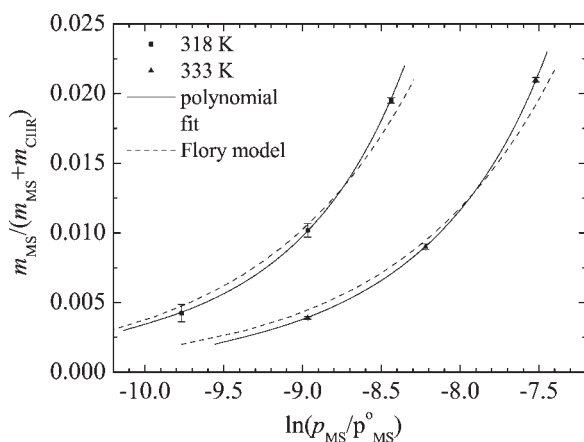*Correspondence to:* E. Bakken (egil.bakken@sintef.no).
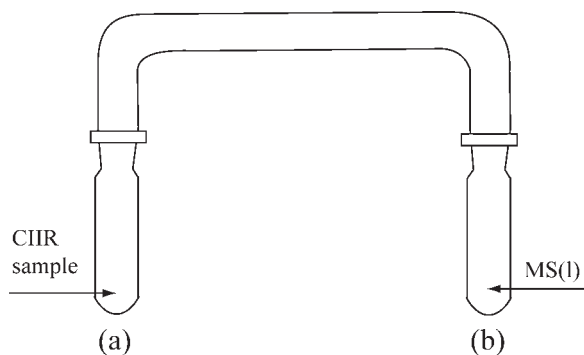
Figure 1 Glass set-up where CIIR in tube (a) is exposed to MS(g) by heating MS(l) in tube (b).

the absorption measurements was almost entirely due to uptake of MS(g). However, small amounts of water and plasticizers from the sample were still exchanged with the surroundings and corrections were made by monitoring the weight change of a reference sample. The reference sample was exposed to the same conditions as the samples, except for the MS vapor, and it was assumed that the sample and the reference sample exchanged the same amount of water and plasticizers.
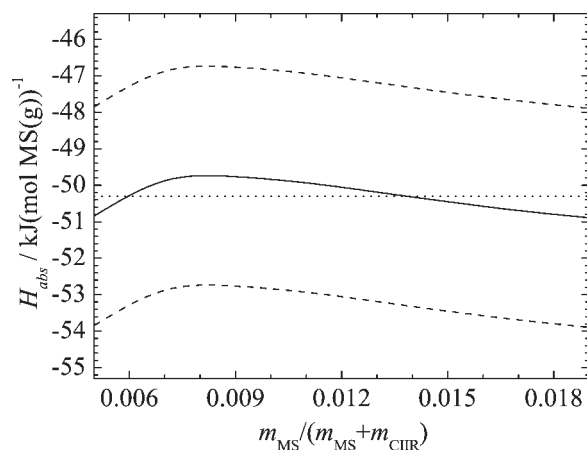
RESULTS AND DISCUSSION

Solubility and sorption energetics

Figure 2 shows the measured solubilities of MS in CIIR at 318 and 333 K at various MS vapor pressures. The ordinate gives the equilibrium weight fraction of MS in CIIR, and the abscissa gives the natural logarithm of the equilibrium vapor pressure of MS relative to the standard pressure ($^{\mathrm{o}} \equiv 1$ bar). The estimated uncertainties are half of the amount of water and plasticizers that the samples exchanged with
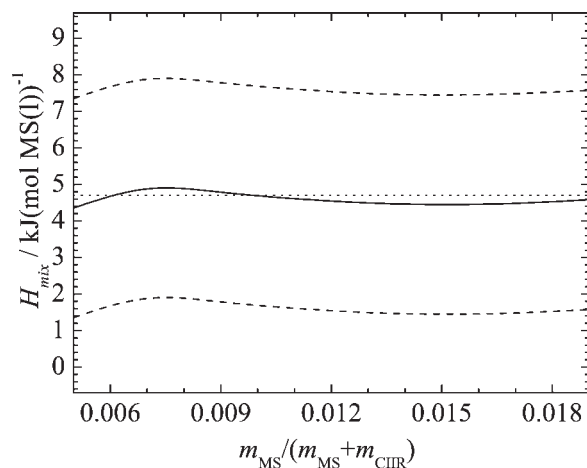

Figure 3 Enthalpy of absorption (solid line) derived from eq. (1) and the polynomials fitted to the experimental data. The dashed lines are estimated uncertainties, and the dotted line gives the enthalpy of absorption that is regarded as independent of concentration.

the surroundings. The partial molar enthalpy of absorption, H_{abs}, of MS(g) in CIIR and the partial molar enthalpy of mixing, H_{mix}, of MS(l) in CIIR are derived from the present solubility data, see Figures 3 and 4, respectively. H_{abs} is obtained by a linear fit of eq. (1)

$$\ln\left(\frac{p_{\mathrm{MS}}}{p_{\mathrm{MS}}^{\mathrm{o}}}\right) = \frac{\mu_{\mathrm{MS}} - \mu_{\mathrm{MS}}^{\mathrm{o}}}{RT} = \frac{H_{\mathrm{MS}} - H_{\mathrm{MS}}^{\mathrm{o}}}{RT} - \frac{S_{\mathrm{MS}} - S_{\mathrm{MS}}^{\mathrm{o}}}{R}$$

(1)

versus $1/T$ to the experimental data in Figure 2. μ_{MS}, H_{MS}, S_{MS}, and p_{MS} in eq. (1) are the partial molar Gibbs energy, enthalpy, and entropy of MS in CIIR and the partial pressure of MS, respectively. $\mu_{\mathrm{MS}}^{\mathrm{o}}$, $H_{\mathrm{MS}}^{\mathrm{o}}$, $S_{\mathrm{MS}}^{\mathrm{o}}$ and $p_{\mathrm{MS}}^{\mathrm{o}}$ are the standard partial molar Gibbs energy, enthalpy, and entropy of MS and the standard

Figure 2 Measured equilibrium weight fractions of absorbed MS in CIIR versus MS vapor pressures at 318 (■) and 333 K (▲). The solid lines are polynomials fitted to the experimental data, and the dashed lines are the Flory model derived from the present enthalpy of mixing.

Figure 4 Enthalpy of mixing (solid line) derived from eq. (1) and the polynomials fitted to the experimental data. The dashed lines are estimated uncertainties, and the dotted line gives the enthalpy of mixing that is regarded as independent of concentration.

pressure of MS(g), respectively. Equation (1) can be found in physical chemistry text books,[12] and it is derived by noticing that the partial molar Gibbs energy of MS in CIIR and in the surrounding gas phase are equal at equilibrium. Note that H_{mix} is calculated from eq. (1) when the standard state of the partial, molar quantities is changed from 1 bar (°) to the saturation pressure (*) of the MS vapor.

The two enthalpies

$$H_{abs} = H_{MS} - H_{MS}^o \qquad (2)$$

and

$$H_{mix} = H_{MS} - H_{MS}^* \qquad (3)$$

are calculated from the slopes of the straight lines given by eq. (1). To obtain H_{abs} and H_{mix} at a larger number of concentrations, the measured data were interpolated according to the fitted polynomials in Figure 2.

The variations of H_{abs} and H_{mix} versus MS concentration are given by the solid lines in Figures 3 and 4, respectively. The estimated uncertainties are given by the dashed lines in the same figures. The small variations of the enthalpies do not seem to follow a physical trend and are probably due to experimental uncertainties and the interpolation of the data. The two enthalpies are correlated since they are derived from two data sets that only differ by a change in the standard state of the MS vapor. Hence, it is assumed here that both H_{abs} and H_{mix} are almost constant in the present concentration interval, and are thus well described by the dotted, straight lines in Figures 3 and 4, respectively. The obtained enthalpies are $H_{abs} = -50.3 \pm 3$ kJ (mol MS(g))$^{-1}$ and $H_{mix} = 4.7 \pm 3$ kJ (mol MS(l))$^{-1}$.

The present results show that $|H_{abs}| \gg H_{mix}$ and the major contribution to the enthalpy of absorption, $H_{abs} = H_{mix} - H_{vap}$, is the enthalpy of condensation ($-H_{vap}$). This is a common feature for many vapor–polymer systems.[13] As mentioned earlier, MS(l) and HD(l) have similar vapor pressures,[3,4] and thus similar H_{vap}, and MS is therefore a promising candidate to simulate the enthalpy of absorption of HD in CIIR.

Solution thermodynamics

The Flory model[14,15] describes the equilibrium partial pressure of a penetrant (p_{MS}) in a polymer material (CIIR) according to

$$\ln\left(\frac{p_{MS}}{p_{MS}^*}\right) = \ln v_{MS} + \left(1 - \frac{V_{MS}}{V_{CIIR}}\right)v_{CIIR} + \chi v_{CIIR}^2 \qquad (4)$$

V_{MS}, V_{CIIR}, v_{MS}, and v_{CIIR} in eq. (4) are the partial molar volume of MS and CIIR and the volume frac-

TABLE I
Calculated Flory Interaction Parameter, χ, as a Function of Temperature and Weight Fraction, $w_f = m_{MS}/(m_{MS} + m_{CIIR})$, of MS in CIIR

T (K)	χ						
	0.003[a]	0.006	0.009	0.012	0.015	0.018	0.021
318	1.79	1.80	1.81	1.82	1.83	1.84	1.85
333	1.71	1.72	1.73	1.74	1.75	1.76	1.77

[a] 0.003, 0.006, 0.009, 0.012, 0.015, and 0.021 are weight fractions of MS in CIIR, respectively.

tion of MS and CIIR, respectively. The Flory interaction parameter, χ, in eq. (4) is related to the enthalpy of mixing by Ref. 14.

$$H_{mix} = RT\chi v_{CIIR}^2 \qquad (5)$$

Equation (5) shows that the interaction parameter can be obtained directly from the present H_{mix} in Figure 4. Table I gives some calculated values of χ, and it is shown that χ decreases with temperature and increases with MS concentration. Hence, at the standard temperature (298 K), it is expected that both the solubility of MS in CIIR and the Flory interaction parameter increase compared to the results measured at 318 and 333 K in this work.

To compare the present solubility data with the Flory model, the standard state in eq. (4) was changed to 1 bar (°). The dashed lines in Figure 2 show that the present measurements agree well with the Flory solution theory. All the parameters in the Flory model are known from experiments, and the agreement between the data and the model was thus obtained without fitting any of the parameters.

The Flory model assumes a random distribution of the absorbed molecules in the polymer, and deviations from this ideal behavior are presently included in the enthalpic term, χ. In a more sophisticated treatment, the Flory model also includes a (nonconfigurational) entropic term[14–16] that describes the temperature dependence of the (nonconfigurational) energy of mixing. However, the simpler model used here satisfactorily predicts the solubility of MS in CIIR in the present temperature and concentration interval.

CONCLUSIONS

This work presents solubility measurements of MS in CIIR at 318 and 333 K. The enthalpy of absorption of MS(g) in CIIR and the enthalpy of mixing of MS(l) in CIIR are derived from the experimental data. It is shown that the main contribution to the enthalpy of absorption is the enthalpy of condensation. The Flory model describes the observed solubilities well when

the Flory interaction parameter is calculated from the measured enthalpy of mixing.

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