Sorption of high pressure fluid mixtures into semi-crystalline polymers: investigation of the system carbon dioxide/vinylidenefluoride/poly(vinylidenefluoride)

To cite this article: A Cipollina et al 2008 J. Phys.: Conf. Ser. 121 022020

View the article online for updates and enhancements.

You may also like

- The metal/organic interface in cobalt/vinylidene fluoride heterostructures
  K Foreman, E Echeverria, M A Koten et al.

- Effects of M220 on the crystal structure and dielectric properties of P(VDF-HFP)
  Yajing Bai, Guirong Peng, Xiaojia Zhao et al.

- Poly(vinylidene fluoride-hexafluoropropylene) based blend film for ultrahigh energy density capacitor applications
  Jinxi Zhang, Xinyu Du, Chenchen Wang et al.
Sorption of high pressure fluid mixtures into semi-crystalline polymers: investigation of the system carbon dioxide/vinylidene fluoride/poly(vinylidene fluoride)

Andrea Cipollina, Alessandro Galia, Onofrio Scialdone, Giuseppe Filardo
Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo
galia@dicpm.unipa.it

Abstract. A novel experimental apparatus for measuring gas absorption has been adopted to study sorption of carbon dioxide CO$_2$ and vinylidene fluoride (VDF) in a semi crystalline polymer, namely poly(vinylidene fluoride) (PVDF). The experimental technique allows to calculate simultaneous absorption of different components in the polymer phase, through a gas chromatographic determination of the composition of the fluid phase. To take into account indirectly the polymer swelling, a suitable not-absorbable probe, namely argon, has been added to the fluid phase. Concentrations of molecules absorbed in the polymer phase were simply calculated through mass balance equations written for each component in the two phases. Several different operating conditions were investigated. Temperature was kept constant at 50°C, while pressure varied between 8 and 35 MPa. Sorption was measured for pure CO$_2$ and VDF and for mixtures containing around 0.20 w/w and 0.40 w/w of VDF in CO$_2$, to analyse how the presence of a different component could affect the sorption of the other. Results show that pure CO$_2$ presents a solubility more than three fold higher than pure VDF at the same pressure conditions. On the other side, when both gases were present in the mixtures, the sorption of CO$_2$ seems to be strongly inhibited by VDF, whereas this latter presents a solubility quite similar to the pure gas if operating at the same partial pressure.

1. Introduction
The interest in measuring sorption of dense gases in a polymer phase has been rising in the last years, due to the importance of characterizing the gas sorption during polymerization processes in supercritical fluids, in membrane separation technology, in the devolatilization of solvents in as-polymerized macromolecular matrixes, etc.. Indeed, several experimental methods have already been described in the literature to study sorption and swelling of polymers contacted with high pressure fluid systems. Some of them are based on the measurement of the pressure decay accompanying the sorption of the gaseous compound inside the matrix [1], others are substantially in-situ gravimetric techniques such as the quartz spring method originally adopted at pressures lower than 10 MPa by R. G. Wissinger and M. E. Paulatis [2] and later extended to more dense supercritical systems. [3] Similar approaches are based on the utilization of electro [4], micro [5] or mass suspension [6-7] balances to perform the weighting of the polymer sample directly in the dense fluid atmosphere. More sophisticated approaches based on the measurement of the resonant frequency of a suitable mechanical
system made solidal to the polymer specimen and immersed in the supercritical phase have been proposed also. [8]

All these techniques share a common drawback even if at different level: all of them suffer of the uncertainty arising from the difficulty of evaluating the volume dilation of the polymer sample during the sorption measurements. This can be a relevant source of error in the evaluation of the solubility of the penetrant. Moreover they cannot be used to measure sorption of penetrants in multi-component systems as it is difficult to separate the effect of the absorption of different compounds.

On the basis of these considerations, the aims of the present work was to investigate the sorption of supercritical fluid mixtures containing carbon dioxide (CO$_2$) and vinylidenefluoride (VDF) in poly(vinylidenefluoride) (PVDF) using a gas chromatographic experimental approach. This experimental technique, already presented for the case of sorption of a pure component [9], allows for the sorption measurement taking into account intrinsically the effect of the swelling of the polymer and can be used in the presence of multi-component fluid systems. For this reason a small amount of Argon, a not absorbable gas to be used as GC internal standard, was added in the gaseous phase. The amount of CO$_2$ and VDF dissolved in the polymer is determined by solving the mass balance equations written for each component (CO$_2$, VDF and probe) using their relative concentration evaluated by gas chromatographic analyses of the gaseous mixture after attainment of equilibrium.

2. Materials and method

PVDF Solef 1010, cristallinity 55%, under the form of cylindrical pellets (diameter d=3 mm, d/h=1), and VDF were kindly donated by Solvay Solexis. Prior to the insertion in the sorption vessel the polymer was pretreated in a vacuum oven by heating at 140 °C for 3 h and then slowly cooled down to room temperature (cooling time 3-5 hours). The adopted CO$_2$ was Air Liquide 99.998 pure, Ar was Air Liquide 5.0. Both gases were used without further purification. The gas chromatographic analyses were carried out by a Hewlett Packard Serie HP 6890 GC, equipped with a Carboxen TM-1000 separation column and a thermal conductivity detector (TCD), and Hydrogen 6.0 produced by a Parker electrolytic gas generator was used as carrier gas.

The experimental apparatus was assembled using commercial elements and is schematically depicted in Figure 1. It consists of a high pressure sorption cell (PARR vessel Model 2670 with nominal free volume 72 mL) fitted with a high pressure transducer (Sensotec Model: STJE/1890-20A) with accuracy ± 0.05 MPa. The sorption cell is inserted in a closed circuit prepared with 1/16 inch OD AISI 316 tubing and equipped with a six-ways high pressure sampling valve (Rheodyne valve Model 7000). The switching valve was added to allow the real time sampling of the fluid phase contacted with the polymer and to this purpose two ports of the valve are connected with a 6µl high pressure sampling loop while other 2 ports are connected to the carrier line (H$_2$) of the gas chromatograph. The GC carrier circuit was modified to use the hydrogen itself, available at 0.5 MPa from the gas generator, to entrain the fluid contained in the sample loop to the chromatographic column. Mixing in the sorption cell was obtained by a high pressure magnetic driven gear pump (5), Micropump® model GAH-V21-C, which allowed circulation flow rates up to 100 ml/min at operating conditions, thus guaranteeing very short mixing times.

![Figure 1. Sketch of the sorption cell and auxiliaries.](image-url)
3. Results and discussion

The amount of compounds dissolved in the polymer is determined from the evaluation of gaseous components concentrations (CO\(_2\), VDF and probe) in the fluid phase, obtained considering a homogeneous system, by GC measurements. In particular, the amount of CO\(_2\) and VDF absorbed into the polymer can be computed by the mass balance equations of the three components (eqs. 1-3) properly combined (eqs. 4, 5).

\[
\begin{align*}
M^°_{CO2} &= M^P_{CO2} + \omega^g_{CO2} [V-V^o_P - V^{sw}_P] \\
M^°_{VDF} &= M^P_{VDF} + \omega^g_{VDF} [V-V^o_P - V^{sw}_P] \\
M^°_{Probe} &= \omega^g_{Probe} [V-V^o_P - V^{sw}_P]
\end{align*}
\]

where \(V\) = reactor volume; \(V^o_P\) = initial volume of the polymer; \(V^{sw}_P\) = swelling volume; \(M^0_i\) = initial masses (weighted); \(M^P_i\) = mass absorbed in the polymer; \(\omega^g_i\) = equilibrium concentrations in the fluid phase.

\[
\begin{align*}
M^P_{CO2} &= M^0_{CO2} - \left(\frac{\omega^g_{CO2}}{\omega^g_{Probe}}\right)M^0_{Probe} \\
M^P_{VDF} &= M^0_{VDF} - \left(\frac{\omega^g_{VDF}}{\omega^g_{Probe}}\right)M^0_{Probe}
\end{align*}
\]

A crucial point for the accuracy and precision of our technique is the selection of the compound that must be used as a probe. An ideal probe should have the following features:

1) it must be absorbed in a negligible way into the polymer phase;
2) it must negligibly modify chemical potentials of the other species dissolved in the gas mixture;
3) it must be completely miscible with other components of the fluid phase under adopted experimental conditions and must be detectable by TCD using H\(_2\) as a carrier.

Argon was selected as a probe since we have estimated, by Berens approach, that at 200 bar and 40°C its solubility in the polymer is in the range of 0.001÷0.002 gr/gr of PVDF. [9] Moreover, using the Peng & Robinson EOS, the effect of the noble gas on chemical potentials of the other components was found negligible provided that its mole fraction in the fluid phase is kept lower than 0.05. [9]

All the experiments were performed loading the polymer and the gaseous components and then heating the system at 50°C leaving it with a proper mixing for about 24 hrs in order to achieve equilibrium conditions. Eventually several GC analysis (at least 5 analysis) were performed to measure the fluid phase composition in order to verify the achievement of equilibrium.

Sorption values for the pure components were measured first and are reported in Figs. 2 and 3:

![Fig.2 Sorption measurements for pure CO\(_2\) at 50°C compared with literature data at 40°C.](image1)

![Fig.3 Sorption measurements for pure vinylidenefluoride at 50°C.](image2)

The two figures indicate that higher sorption values are achieved by pure CO\(_2\), with a maximum of about 25 gr of CO\(_2\) per 100gr of amorphous PVDF achieved at about 340 bar of total pressure. VDF presents a much smaller solubility in PVDF, achieving sorption values slightly higher than 5gr of VDF per 100gr of amorphous polymer at similar pressure conditions.
Sorption measurements for fluid mixtures were performed with mixtures containing CO$_2$ and VDF at mass ratios of 80/20 and 60/40, which are reported in Figs. 4 and 5 with reference to the sorption of CO$_2$ and VDF respectively. Interestingly, at the same values of partial pressure sorption of CO$_2$ is significantly reduced by the presence of VDF, which therefore acts as inhibitor. On the other side, VDF sorption values seem to be strongly dependent on the partial pressure, being not markedly influenced by the presence of CO$_2$.

**Fig.4** CO$_2$ sorption vs P$_{CO2}$ for the pure component and the two mixtures (CO$_2$/VDF weight ratio of 60/40 and 80/20) at 50°C.

**Fig.5** VDF sorption vs P$_{VF2}$ for the pure component and the two mixtures (CO$_2$/VDF weight ratio of 60/40 and 80/20) at 50°C

**Conclusions**
A novel experimental method to measure sorption of supercritical fluid mixtures inside polymers was used to study the solubility of supercritical CO$_2$ and VDF in PVDF. The technique is based on the use of a gas chromatograph to determine the equilibrium composition of the fluid phase contacted with the polymer. These data, obtained with the use of a purposely selected inert probe (Argon), are used to solve the algebraic system of mass balance equations of the components that partition between the two phases. Results have shown that both pure CO$_2$ and VDF adsorb in PVDF, although sorption values for CO$_2$ arrive up to about 25gr per 100gr of amorphous polymer, while solubility of VDF is only slightly higher than 5gr per 100gr of amorphous polymer at pressures around 35 MPa. When the two gases are present in mixtures lower sorption values were measured, indicating in particular an anti-solvent effect of VDF on CO$_2$ solubility, which is highlighted by the much lower sorption values achieved by CO$_2$ in mixtures when compared to the sorption of the pure gas at similar value of partial pressure.

**References**
[1] Stern S A and De Meringo AH 1978 J. Polym. Sci., Polym. Phys. Ed. 16 735
[2] Wissinger R G and Paulatis M E 1987 J. Polym. Sci. Part B: Polym. Phys. 25 2497
[3] Chang S H, Park S C and Shim J J 1998 J. Supercrit. Fluids 13 113
[4] Kamiya Y, Hirose T, Mizoguchi K and Naito Y 1986 J. Polym. Sci. Part B 24 1525
[5] Kikic I, Lora M, Cortesi A and Sist P 1999 Fluid Phase Equilibria 158-160 913
[6] Von Schnitzler J and Eggers R 1999 J. Supercrit. Fluids 16 81
[7] Rajendran A, Bonavoglia B, Forrer N, Storti G, Mazzotti M and Morbidelli M 2005 Ind. Eng. Chem. Res. 44 2549
[8] Bonner D C and Cheng Y J 1975 J. Polym. Sci. Polym. Lett. Ed. 13 259
[9] Galia A, Abduljwad M, Scialdone O and Filardo G 2006 AIChE Journal 52 2243