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A new prediction method for organic liquids sorption into polymers

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ABSTRACT

A new prediction method for sorption of low-molecular organic liquids (non-solvents) in polymers is presented. It was derived from the gravimetric data for sorption of linear and cyclic alkanes, aromatics and alcohols into various kinds of polymers (glassy polystyrene, rubbery polydimethylsiloxane, semicrystalline low-density polyethylene, ion exchange Nafion, and copolymeric poly(styrene-butadiene-styrene) in temperature range 5–50 °C. Our method is based on a normalised function $\varphi_Q(t)$ evaluated from series of the equilibrium mass swelling degrees Q_m of a model liquid in one polymer at each temperature from the indicated temperature interval to the corresponding Q_m at the highest temperature of this interval. A knowledge of the proper function $\varphi_Q(t)$ for given polymer enables to predict a sorption of any other liquid with the same properties or interactions with given polymer in given temperature range just from a knowledge of a single experimental Q_m value at any temperature from the indicated temperature interval. The steepest temperature dependent normalised function $\varphi_Q(t)$ exhibited LDPE+liquid systems. Contrarily, PDMS+liquid systems were practically temperature independent. The thermodynamic analysis of the sorption process in studied polymer–liquid systems comprised evaluation of the appropriate values of the sorption enthalpy $\Delta_s H$ and the sorption entropy $\Delta_s S$. The values of the resulting Gibbs energy of sorption $\Delta_s G$ were negative in all cases and thus confirmed the spontaneity of liquids sorption in polymers over the whole temperature range.

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1. Introduction

The worldwide plastics utilisation invariably entails deliberated but also unintended contacts with various liquids. Therefore, the detailed knowledge of all potential effects of these actions on material properties of both common plastics and high-quality products for instance LCD-panels, transdermal patches, medical test strips, etc. is essential [1]. Understanding of the thermodynamics of polymer+solvent systems is also important in polymer production processes such as polymerisation, devolatilisation, plasticisation, preparation of tailor made membranes for special applications, etc. [2].

The process of sorption of organic liquid into a polymer matrix is driven via the gradient of chemical potential of penetrant until the thermodynamic equilibrium in the polymer–liquid system is reached. Typical sorption process can be easily detected and quantified gravimetrically as a weight increase of the sorbent (polymer) [3]. Usually, such mass uptake is presented in the form of the equilibrium mass swelling degree Q_m [4,5], i.e. the relative

difference between dry and (moist) swollen polymer:

$$Q_m = \frac{m_{LP} - m_p}{m_p} \quad (1)$$

where m_p and m_{LP} are the weights of the dry and swollen polymer, respectively.

Generally, the properties of polymers, liquids and their mutual interactions are more or less influenced by the temperature. Therefore, a gravimetric sorption of non-solvent liquids into one kind of polymer can be divided into three cases: (i) sorption increases with increasing temperature, (ii) sorption decreases with increasing temperature, or (iii) sorption can be in specific temperature range completely temperature-independent. Our prediction method can be used in (i) and (ii) cases, however only in the situation, when sorption of all liquids in specific polymers follows the same trend (the same case). This means that studied liquid must be a non-solvent for given polymer, i.e. only the mild interactions between polymer and liquid should take place, and its sorption must be reasonable (not less than circa 0.01 g/g). Moreover, the sorption of liquids in given polymer should not be temperature independent.

In this work, presented results of the liquid sorption of linear and cyclic alkanes, aromatics and alcohols in glassy polystyrene (PS), rubbery polydimethylsiloxane (PDMS), semicrystalline low-density polyethylene (LDPE), ion exchange Nafion (N115), and

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copolymeric polystyrene–butadiene–styrene (SBS) in temperature range 5–50 °C enabled to formulate a new prediction method for sorption of non-solvents in polymers. The main topic of this work, the sorption of organic liquids into various polymers, has been continuously investigated in our laboratory over the past several years [4–9]. Based on our experiences, a motivation for this paper was to bring a new insight into the liquid sorption-related phenomena, and, last but not least, to improve the current understanding of the sorption process in a wider context.

1.1. Thermodynamics of the sorption process

Similarly to a chemical reaction, the process of sorption of liquid L in polymer P can be described as



where LP represents a swollen polymer, i.e. a polymer which comprises sorbed liquid. At sorption equilibrium, it is possible to describe the sorption process analogously to the standard thermodynamics of chemical reaction as

$$\Delta_s G^\ominus = -RT \ln K_{LP} = \Delta_s H^\ominus - T\Delta_s S^\ominus \quad (3)$$

where $\Delta_s G^\ominus$ is the Gibbs energy of sorption process, $\Delta_s H^\ominus$ is the enthalpy of sorption process (the change of the system enthalpy corresponding to the thermodynamic process of dissolving one mole of penetrant, which is usually interpreted as a measure of the strength of polymer–penetrant energetic interactions), $\Delta_s S^\ominus$ is the entropy of sorption process, R is the universal gas constant, and T is the temperature of sorption.

The equilibrium constant K_{LP} , which represents a polymer–liquid system in the sorption equilibrium, can be expressed by

$$K_{LP} = \frac{a_{LP}}{a_p \cdot a_L} \quad (4)$$

where $a_p = 1$ is an activity of polymer (standard state – dry pure polymer at temperature and pressure of the process), and $a_L = 1$ is an activity of liquid (standard state – pure liquid at temperature and pressure of the process). All quantities are related to 1 g of the dry polymer. The activity of the swollen polymer a_{LP} can be calculated as

$$a_{LP} = \frac{m_{LP}}{m_p} \quad (5)$$

The conception of equilibrium constant of the sorption process K_{LP} was firstly introduced by Aminabhavi et al. [10,11]. However, their definition of activity of polymer–liquid system a_{LP} is incorrect from the thermodynamical point of view. They defined activity of a swollen polymer a_{LP} in sorption equilibrium based only on equilibrium liquid uptake by polymer $a_{LP} = (m_{LP} - m_p)/m_p$. Contrariwise, our definition of a_{LP} reflects a reality because we define it via swollen polymer that comprises both phases in sorption equilibrium, sorbed liquid and solid polymer.

1.2. Prediction methods in literature

Basically, a plenty of experimental methods for the material properties are time and cost consuming. Existing predictive methods for a liquid sorption in polymers are often inadequate and cannot be used universally. For example, a combination of the Cosmo-SAC model and the Flory–Rehner equation was reported recently [12] but such model performs poorly in the case of some polar solvent/polar polymer combinations. While this method is not sound from a fundamental viewpoint, it may be practically useful in predicting of two component sorption from single component sorption data. Other researchers combined BET and GAB equations [13] for water sorption in foodstuffs. Different materials were tested and the prediction capability of the GAB

model was verified with very good results but only for water vapours in the activity range between 0 and 0.95. Unfortunately, no results of its application to the sorption of liquids are reported.

The prediction of sorption and permeation flux of liquids in PDMS for pervaporation process design was reported by Oh et al. [14]. Their prediction method does not include any adjustable parameters for the polymer or solvent; for good solvents the calculated values were in fairly good agreement with experimental data, but it was inadequate to provide relevant results for poor solvent.

By contrast, our prediction method is simple and versatile. It can be used for different types of polymers and non-solvent liquids in certain temperature range under previously mentioned conditions. The uniqueness of our method consists in fact that it enables to predict a sorption of non-solvent liquid in given polymer at different temperatures just from its single experimental point at one temperature using the proper normalised sorption function obtained from the sorption of the other non-solvent(s).

2. Experimental

2.1. Materials and chemicals

High-pressure low density polyethylene (LDPE) BRALEN FB 2-30 (Slovnaft, Bratislava) in the form of foil (thickness 0.046 mm – measured by an Inductive Dial Indicator, Mahr, Germany) was used. Its density ($\rho = 0.940 \pm 0.002 \text{ g cm}^{-3}$) was determined by weighing of the sample of known area and thickness. The degree of crystallinity was reported to be 45% [7].

Polydimethylsiloxane (PDMS) RTV 8335 (Momentive Performance Materials, USA) [15] membrane was prepared from two components (base and crosslinker). The base was mixed with pentane and then the crosslinker was added. During the following vulcanisation all pentane evaporated. The final product of this process was colourless rubbery membrane. Its density ($\rho = 1.069 \pm 0.003 \text{ g cm}^{-3}$) was determined by weighing of the sample of known area and thickness.

Styrene–butadiene–styrene block copolymer (SBS, Kraton Polymers) is a linear triblock copolymer with 28% styrene. A combination of rigid styrene blocks with flexible butadiene chains is reflected in excellent material properties, for instance good chemical stability, enormous tensile strength and surface friction coefficient, outstanding electrical properties and great workability. Its density (1.87 g cm^{-3}) was determined by weighing of the sample of known area and thickness.

Nafion N-115 (DuPont) was used as received. Nafion is a poly (tetrafluoroethylene) (PTFE) polymer with perfluorovinyl pendant side chains ended by sulphonic exchange groups [16]. The sulphonic exchange groups on the side chains have very high acidity. Thickness of foil 0.136 mm was measured by an Inductive Dial Indicator Mahr; density $1.926 \pm 0.004 \text{ g cm}^{-3}$ was determined by weighing of the sample of known area and thickness.

Polystyrene (PS) is one of the most widely used plastics. It is a rather poor barrier to oxygen and water vapour and has a relatively low melting point. PS was purchased from BDH [17]. Its density ($\rho = 0.846 \pm 0.003 \text{ g cm}^{-3}$) was determined by weighing of the sample of known area and thickness.

Low-molecular liquids: {i} linear alkanes (hexane); {ii} cyclic alkanes (cyclohexane and methylcyclohexane); {iii} aromatics (benzene, methylbenzene, ethylbenzene, and propylbenzene) and {iv} alcohols (butan-1-ol, butan-2-ol, hexan-1-ol, and cyclopentanol) with p.a. purity grade were purchased from Sigma-Aldrich and were used without further purification.

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