



Sorption phenomena of organic solvents in polymers: Part I

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Received 18 October 2004; received in revised form 25 November 2004; accepted 29 November 2004
Available online 25 January 2005

Abstract

In this work we use the vapor-sorption equilibrium data to show the degree of solvent upturn in each solvent–polymer system. For this purpose, 23 isothermal data sets for four polymer + solvent binaries, one block copolymer + solvent binary and for the corresponding polymer pairs have been used in the temperature range of 25–70 °C. Solvents studied are benzene, carbon tetrachloride, chloroform and pentane. Homopolymers studied are polyisobutylene, poly(ϵ -caprolactone), poly(ethylene oxide), *n*-heptadecane, polystyrene, poly(vinyl chloride), poly(vinyl methyl ether), and *n*-tetracosane.

According to these data sets, solvent weight fraction in the polymer is plotted against solvent-vapor activity that is calculated assuming an ideal gas phase of pure solvent vapor neglecting the vapor pressure of the polymer. We use the Flory–Huggins theory to obtain dimensionless interaction parameter, χ . Also the Zimm–Lundberg clustering theory and non-ideality thermodynamic factor, F are used to interpret the equilibrium data.

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Keywords: Sorption phenomena; VLE data; Flory–Huggins interaction parameter

1. Introduction

Recently the widespread use of polymers and the need for their synthesis has increased the interest and thereby research in the field of polymer solutions. Also due to their technological importance, polymer blends have attracted considerable attention during the past decade. The thermodynamic and physico-chemical properties of polymers are especially relevant in polymer processing and industrial applications [1–4]. Sorption data are pertinent to a variety of applications including packaging and coating technology, membrane separation of gases and vapors, drug-delivery systems, biocom-

patible materials for biomedical applications and contact lens industry [5–8].

For thermodynamic reasons, most polymer pairs are immiscible and their degree of compatibility is of underlying importance to the microphase structure and consequently, to the mechanical properties of the blend. The Flory–Huggins χ interaction parameter for the polymer pair plays a dominant role in explaining critical phase behavior of a compatible pair and in estimating interfacial tension and interfacial thickness for semicompatible or incompatible pairs. Direct measurement of this parameter is not always possible and we use the Flory–Huggins theory to obtain this dimensionless parameter.

The sorption of solvent vapor by polymers often portrays large vapor uptakes and according to the BET classification [9], almost all the polymers exhibit a type III isotherm. Two possible explanations for a large

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Table 1
Summary of polymers with their relevant solvents

Polymer	M_w	V_{sp} (cm ³ g ⁻¹)	Solvent	T (°C)	P_s (kPa)	V_{sp} (cm ³ g ⁻¹)
Polyisobutylene	2700	0.949	Pentane	25	68.333	1.183
Polyisobutylene	1350	0.949	Pentane	25	68.333	1.183
Poly(ϵ -caprolactone)	33,000	0.769	Carbon tetrachloride	65	69.981	0.487
Poly(ethylene oxide)	600	0.753	Benzene	55	43.583	0.895
Poly(ethylene oxide)	100,000	0.753	Benzene	70	73.437 ^a	1.199 ^a
<i>n</i> -Heptadecane	240	1.063	Pentane	25	68.333	1.183
Polystyrene	800	0.810	Chloroform	25	26.222	0.512
Polystyrene	800	0.810	Benzene	25	12.664	0.886
Poly(vinyl chloride)	77,300	0.624	Carbon tetrachloride	65	69.981	0.487
Poly(vinyl methyl ether)	14,000	0.828	Chloroform	25	26.222	0.512
Poly(vinyl methyl ether)	14,000	0.828	Benzene	25	12.664	0.886
<i>n</i> -Tetracosane	338	1.054	Benzene	55	43.583	0.895

^a All values are taken from [12] except this one that is taken from [18].

degree upturn at high activity are clustering of solvent molecules or plasticization of the polymer matrix induced by solvent sorption. In clustering the proportion of clustered molecules increases with increasing sorbed concentration, then it would be expected that the diffusion coefficient of the polymer-penetrant system would decrease with increasing concentration and contrasts with the behavior of sorbed solvents or swelling agents when diffusion increases with concentration that is agreement with the concept of plasticization. Zimm and Lundberg theory [10] provides a method to determine the extent of clustering of the solvent molecule inside the polymer matrix. The advantage of this integral is that it can be obtained directly from equilibrium data.

This paper concerns sorption of some organic solvent vapor on three compatible or semicompatible pairs, one block copolymer system and their parent homopolymers in temperature range 25–70 °C. Table 1 gives a summary of all polymers with their relevant solvents that are considered here.

2. Vapor-sorption equilibria

The ideal solution law, as embodied in Raoult's law, provides the basis for the treatment of simple molecule solution. Although such solutions seldom behave ideally over wide ranges in concentration, the correlation usually is adequate to justify adoption of the classically defined ideal solution as a standard for comparison. Solutions in which the solute is a polymer of high molecular weight exhibit very large deviations from ideality. Only at extreme dilutions where, the ideal law must be approached as an asymptotic limit, does the polymer solution conform approximately with ideality. At concentrations exceeding a few percent, deviations from ideality usually become so great that the ideal law is of little value as a basis for rationally correlating the thermodynamic properties of polymer solutions.

According to Raoult's law, the activity a_1 of the solvent in the solution should equal its mole fraction X_1 . In a binary solution consisting of solvent and a polymer having a molecular weight a thousand times or more that of the solvent, only a very small percentage by weight of the solvent is sufficient to bring its mole fraction X_1 very close to unity. Hence, according to Raoult's law

$$a_1 = \frac{P_1}{P_1^0} \quad (1)$$

the partial pressure P_1 of the solvent in the solution should be very nearly equal to that of the pure solvent P_1^0 over the greater portion of the composition range. Experiments do not confirm this prediction. The underlying basis for the failure of the ideal solution law lies in its use of the mole fraction as the composition variable. It consequently presupposes that the effect of a large polymeric solute molecule on the activity of the solvent should be equal to that of an ordinary solute molecule, which may be no larger than one unit in the polymer chain.

In this paper we have used 23 isothermal vapor-liquid equilibria (VLE) data-sets to show the degree of solvent uptake and to examine the effect of weight fraction of polymer on VLE in each system. According to Eq. (1), solvent activity is calculated assuming an ideal gas phase of pure solvent vapor, i.e., neglecting the vapor pressure of the polymer and then, solvent weight fraction is plotted against this activity.

3. Flory–Huggins theory

The entropy of mixing disoriented polymer and solvent may be obtained, according to the original assumptions pertaining to the lattice model [11, chapter 12],

$$\Delta S_m = -k[n_1 \ln \phi_1 + n_2 \ln \phi_2] \quad (2)$$

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