Effect of Acid–Base Interaction on the Sorption Characteristics of Liquids in Poly(vinylidene fluoride)

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SYNOPSIS

The sorption characteristics of various liquids in poly(vinylidene fluoride) (PVDF) were investigated in relation to the Lewis acid–base interaction between the liquids and the polymer. The sorption amount of various liquids and the sorption selectivity of binary mixtures in PVDF were measured and their characteristics were found to be significantly affected by acid–base interaction. The acid–base interaction was evaluated from the Drago constants of PVDF, which were obtained by extending the Fowkes' method observing the shift of stretching frequency of the carbonyl bond of ethylacetate sorbed in PVDF. The partial molar enthalpy change of mixing at infinite dilution was estimated using the Drago constants of PVDF and used as a parameter explaining the sorption characteristics of liquids in PVDF. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

The sorption characteristics of various liquids in a polymer are affected by the intermolecular interactions between the polymer and the liquid sorbates. For nonpolar or weakly polar systems where the intermolecular interactions are restricted to the London dispersive force, the thermodynamics of the sorption process may be well interpreted by the Hildebrand solubility parameter.[1] For more polar systems, specific polymer–liquid interactions may contribute significantly to the sorption characteristics. It is necessary to understand more clearly the effect of specific interactions on the sorption characteristics.

Fowkes et al.[2] suggested that the intermolecular interactions of polymer with neighboring molecules could be determined by considering the London dispersion force and Lewis acid–base interaction. The interaction energy due to the London dispersion force has been quantified by its contribution to the solubility parameter or to the surface energy. The Lewis acid–base interaction energy has been quan-

tified by the Drago correlation[3,4]:

$$-\Delta H^{ab} = E_A E_B + C_A C_B \qquad (1)$$

where the $-\Delta H^{ab}$ is the enthalpy change of the acid–base complexation, and the Drago constants C_A and E_A are the measure of acid strength, and C_B and E_B, the measure of base strength. Fowkes et al.[2] pioneered the determination of the Drago constants of ethylacetate and poly(methyl methacrylate) (PMMA) using the shift of the carbonyl stretching frequency of ethylacetate diluted in solvents or of 3% PMMA dissolved in solvents. In this study, however, the shift of the carbonyl stretching frequency of ethylacetate sorbed in the poly(vinylidene fluoride) (PVDF) having no carbonyl bond was measured. It is believed that the ethylacetate molecules sorbed and diluted in the polymer can interact with the neighboring polymer molecules in the same manner as do the molecules diluted in a solvent. Therefore, the Drago constants of PVDF could be determined using the same correlations suggested by Fowkes et al.[2] for the ethylacetate molecules diluted in a solvent. PVDF was selected as the sorbent because it has acidic property as well as high solvent resistance. The sorption amount and the sorption selectivity of various liquids in PVDF were measured and their characteristics were interpreted in terms of acid–base interaction.

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EXPERIMENTAL

FTIR Measurement

The membranes (thickness: ca. 54 μm) were prepared by casting of 20 wt % PVDF solution in N,N-dimethylformamide and evaporating the solvent for 12 h at 80°C. The prepared membranes were dried *in vacuo* for 48 h at 40°C. The membrane was immersed into ethylacetate. At equilibrium, the membrane was removed and surface liquids were blotted and then the wave number of the carbonyl bond of ethylacetate was measured by FTIR (Bomem, model MB102) with a resolution of 2 cm^{-1}.

Sorption Characteristics

The polymer specimens (thickness: ca. 1 mm) for measuring sorption characteristics were prepared by compression molding with PVDF powder (Aldrich 18,270-2) under the condition of 1,500 psi and 200°C. The crystallinity of the specimen measured by DSC (differential scanning calorimeter, DuPont 910 system) was 47 wt %, which was calculated on the basis of the heat of fusion of 6.7 kJ/mol for the pure crystals.[5]

The dried specimens of PVDF were immersed into the bottles containing the sample of liquids. The bottles were placed in a thermostatically controlled water bath (±0.1°C). At specified time intervals, the specimens were removed from the bottles and surface liquids were blotted with tissue paper and then the specimens were weighed to 0.1 mg using the well-sealed weighing bottles. When there is no detectable gain in weight, the specimens were placed into the desorbing bottle and the liquids sorbed in the strips were desorbed completely through evacuation by heating them from room temperature up to 200°C. The desorbed vapor was collected in the liquid nitrogen trap and its composition was analyzed by gas chromatograph (Varian 1420) fitted with Porapak Q column and a thermal conductivity detector.

RESULTS AND DISCUSSION

Sorption Characteristics of Liquid Mixtures in PVDF

To examine the effect of acid–base interaction on the sorption characteristics of binary mixtures in PVDF, three combinations between liquid mixtures containing 1,4-dioxane as a base liquid were tested—
A: 1,4-dioxane (1)/cyclohexane (2) (base/neutral);

B: 1,4-dioxane (1)/ethanol (2) (base/acid); and C: 1,4-dioxane (1)/ethylacetate (2) (base/base). The acid/base nature of the liquids was made by following Drago et al.[3,4] Figure 1 shows the sorption isotherms of 1,4-dioxane (base) in PVDF. In mixtures A and B, 1,4-dioxane was sorbed preferentially. In mixture C, however, there is no significant preferential sorption, because both liquids are entirely bases. Figure 2 shows the effect of the concentration of 1,4-dioxane in the mixtures on the total sorption wt % (weight gain/weight of dry polymer × 100) in PVDF. In mixtures A and B, the total sorption wt % depends on the concentration of 1,4-dioxane. In mixture C, however, since both liquids are bases, the total sorption wt % is high and varies slightly for the entire range of concentration. These experimental results show that the acid–base interaction may greatly affect the sorption characteristics of liquid mixtures in PVDF.

Determination of Drago Constants of PVDF

To characterize the acidity of PVDF, its Drago constants were determined from the frequency shift of the carbonyl bond in ethylacetate interacting with the polymer. The stretching frequency of the carbonyl bond of the sorbed ethylacetate in the PVDF membrane is shown in Figure 3. In the initial stage of the IR measurement, two distinct peaks (1742 and 1733 cm^{-1}) appear. In the later stage, however, only one peak (1734 cm^{-1}) remains. In the initial
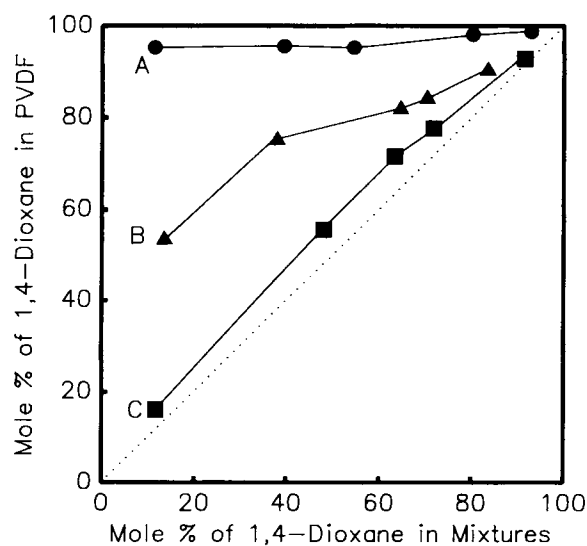

Figure 1 The sorption isotherms of 1,4-dioxane in PVDF at 298.15 K: (A) 1,4-dioxane (1)/cyclohexane (2) (base/neutral); (B) 1,4-dioxane (1)/ethanol (2) (base/acid); (C) 1,4-dioxane (1)/ethylacetate (2) (base/base).

Figure 2 Total sorption wt % (total weight gain/weight of dry polymer × 100) of binary liquids in PVDF as a function of concentration of 1,4-dioxane in the mixtures at 298.15 K: (A) 1,4-dioxane (1)/cyclohexane (2) (base/neutral); (B) 1,4-dioxane (1)/ethanol (2) (base/acid); (C) 1,4-dioxane (1)/ethylacetate (2) (base/base).
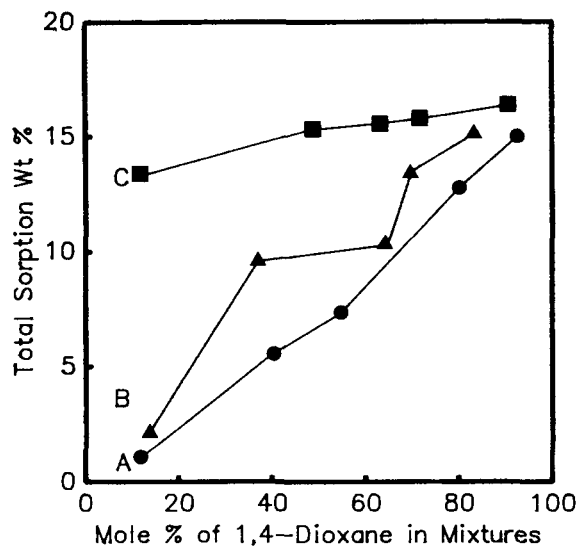
stage, where the concentration of the sorbed ethylacetate in PVDF is high (about 10 mol % of the polymer), two distinct peaks appear for two kinds of ethylacetate molecules: one for the molecules interacting with PVDF (1733 cm^{-1}) and the other for the molecules noninteracting with the polymer (1742 cm^{-1}). The peak for the noninteracting molecules (1742 cm^{-1}) is very close to that for the ethylacetate in the liquid state (1743 cm^{-1}). In the later stage, where the concentration of ethylacetate in the polymer is very low (less than 1 mol %), the noninteracting molecules of ethylacetate disappear and only the molecules interacting with the polymer remain. The remaining molecules are believed to be isolated from each other and have specific interactions with the specific sites in PVDF as well as nonspecific interactions with the surrounding polymer molecules. Therefore, the remaining molecules may be affected by the two kinds of interactions in the same manner as are the molecules diluted in a solvent, as suggested by Fowkes et al.[2]: London dispersive force and Lewis acid-base interaction.

Fowkes et al.[2] proposed that the carbonyl stretching frequency (ν_{CO}) of ethylacetate interacting with solvents and acids could be correlated with the dispersive force contribution to the surface tension of solvents (γ_s^d) and the enthalpy change of the acid-base complexation ($-\Delta H^{ab}$):

$$\nu_{CO} = 1764 - 0.675\gamma_s^d \text{ [dyn/cm]}$$
$$+ 4.24\Delta H^{ab} \text{ [kcal/mol]} \quad (2)$$

where the wavenumber of the carbonyl bond in ethylacetate of the vapor state is given as 1764 cm^{-1}. Substituting the wavenumber of the carbonyl bond of ethylacetate interacting with PVDF (1734 cm^{-1}) and the dispersive contribution to the surface tension of PVDF (25 dyn/cm [Ref. 2]) into eq. (2), the enthalpy change of the acid-base complexation ($-\Delta H^{ab}$) can be obtained. The Drago constants (E_A and C_A) of PVDF could be calculated by solving two simultaneous equations [eq. (1)], each of which can be written for each of two bases with E_B and C_B known (in this study, ethylacetate and PMMA). In Table I, the values of E_B and C_B of ethylacetate and PMMA and their acid-base interaction energies ($-\Delta H^{ab}$) with PVDF are shown. Using these data, the E_A and C_A of PVDF could be determined as 1.8 and 0.7 (kcal/mol)$^{1/2}$, respectively.

The Effect of Acid-Base Interaction on the Sorption Characteristics

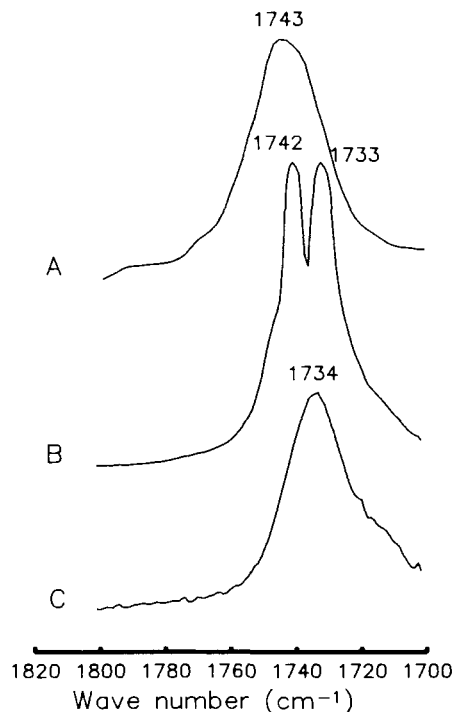The sorption equilibrium is reached when the chemical potential of a liquid inside a polymer is

Figure 3 The infrared spectra of the carbonyl bond of the ethylacetate: (A) pure liquid; (B) sorbed state in PVDF (initial stage, < 1 min); (C) sorbed state (later stage, after 1.5 h).

Table I The Drago Constants (E_B and C_B) of Bases and Their Acid–Base Interaction Energies ($-\Delta H^{ab}$) with PVDF

Bases	E_B (kcal/mol)$^{1/2}$	C_B (kcal/mol)$^{1/2}$	$-\Delta H^{ab}$ (kcal/mol)
Ethylacetate	1.03	1.73	3.1[a]
PMMA	0.68	0.96	1.9[b]

[a] From this study.
[b] From Ref. 2.

equal to that outside the polymer. Many theories have been developed to explain the sorption equilibria of liquids in a polymer based on thermodynamics of mixing. The solubility parameter theory is frequently used[6,7,10] to describe the sorption of a pure component in a polymer. The difference ($\Delta 13$) of the solubility parameter (δ) between a polymer (3) and a sorbate (1) can be used to explain the sorption characteristics for nonpolar or weakly polar liquids:

$$\Delta 13 = [(\delta_{1d} - \delta_{3d})^2 + (\delta_{1p} - \delta_{3p})^2 + (\delta_{1h} - \delta_{3h})^2]^{1/2} \quad (3)$$

where the subscripts d, p, and h denote dispersion force, polar force, and hydrogen bonding, respectively. The Flory–Huggins theory has been widely used[8,9] in interpreting the sorption characteristics. In the theory, the free energy of mixing is obtained using the volume fractions of solvent and polymer and interaction parameters. However, this theory requires a lot of experimental data for the calculation of the interaction parameters.

In this study, the partial molar enthalpy change of mixing at infinite dilution ($\overline{\Delta H_{1\alpha}}$) was used as a parameter explaining the sorption characteristics of liquids in PVDF. Although the $\overline{\Delta H_{1\alpha}}$ does not consider the effect of sorption amount and entropy change of mixing on the sorption characteristics, it could be applied to the interpretation of the sorption in a polymer, because not only is it a relevant parameter to represent the interactions between a liquid and a polymer,[11] but it also requires no data about the sorption. The partial molar enthalpy change of mixing considering acid–base interactions was proposed by Fowkes et al.[2] When the sorption amount of a liquid in a polymer is very low (at infinite dilution), the following equation is obtained:

$$\overline{\Delta H_{1\alpha}} = V_1(\delta_{1d} - \delta_{3d})^2 + \Delta H_{13}{}^{ab} \quad (4)$$

where V_1 is the molar volume of a liquid (1); δ_{1d}, the London dispersion force contribution to the solubility parameter of a liquid (1); and $\Delta H_{13}{}^{ab}$, the Lewis acid–base interaction energy between a polymer (3) and a liquid (1) that could be computed from the Drago correlation. Equation (4) may be useful in explaining and predicting the sorption characteristics of the systems that have an acid–base interaction.

Table II shows the sorption amount (mol %) (mol of liquid sorbed/mol of repeating unit of dry polymer × 100) of various liquids in PVDF. The values of $\overline{\Delta H_{1\alpha}}$ were calculated using the data on the solubility parameter by Hansen and Beerbower[12] for liquids

Table II The Sorption Amount of Pure Liquid (1) in PVDF (3) at 298.15 K

Class	Liquid (1)	Sorption Amount[a]	$\overline{\Delta H_{1\alpha}}$[b] (kcal/mol)	$\Delta 13$[c] (cal/cm^3)$^{1/2}$
Acid	Ethanol	<0.1	0.03	5.4
	Water	<0.1	0.01	16.3
	Chloroform	<0.1	0.01	4.9
Base	Ethylacetate	9	−2.9	3.7
	Acetone	26	−3.4	1.7
	1,4-Dioxane	12	−3.6	5.4
	THF	14	−4.8	3.4
Neutral	Cyclohexane	<0.1	0.01	7.6

[a] Sorption amount (mol %) = (mol of sorbed liquid/mol of PVDF repeat unit) × 100.
[b] $\overline{\Delta H_{1\alpha}}$: Partial molar enthalpy change of mixing at infinite dilution calculated from $\overline{\Delta H_{1\alpha}}$ = $V_1(\delta_{1d} - \delta_{3d})^2 + \Delta H_{13}^{ab}$.
[c] $\Delta 13$: Hansen solubility difference between a liquid (1) and PVDF (3), $\Delta 13 = [(\delta_{1d} - \delta_{3d})^2 + (\delta_{1p} - \delta_{3p})^2 + (\delta_{1h} - \delta_{3h})^2]^{1/2}$.

Table III   The Sorption Selectivity of Binary 50 : 50 Mol % Mixtures in PVDF at 298.15 K

Component (1)	Component (2)	$\alpha_2^{1\,a}$	$-(\overline{\Delta H}_{1\alpha} - \overline{\Delta H}_{2\alpha})$ (kcal/mol)	$\Delta 13/\Delta 23$	$V_1/V_2^{\,b}$
Base	Neutral				
Ethylacetate	Cyclohexane	9	+2.9	0.49	0.91
Acetone	Cyclohexane	19	+3.4	0.23	0.68
1,4-Dioxane	Cyclohexane	20	+3.6	0.71	0.79
Base	Acid				
Ethylacetate	Ethanol	2.6	+2.9	0.70	1.68
Acetone	Ethanol	3.1	+3.5	0.32	1.26
1,4-Dioxane	Ethanol	3.8	+3.6	1.00	1.46
Base	Base				
1,4-Dioxane	Ethylacetate	1.4	+0.6	1.44	0.87

[a] Sorption selectivity, $\alpha_2^1 = (x_1/x_2)_{\text{polymer}}/(x_1/x_2)_{\text{mixture}}$.
[b] Ratio of molar volumes.

and Bottino et al.[13] for PVDF and the Drago constants by Drago et al.[14] for liquids and this work for PVDF. Unfortunately, there may be no pertinent data to be compared with the $-\Delta H_{1\alpha}$ calculated in this study. Galin[11] reported from his inverse gas chromatography study that the $-\Delta H_{1\alpha}$ of ethylacetate in PVDF is 0.5 kcal/mol in the range of 160–210°C, which is much smaller than that (2.9 kcal/mol) of this study at 25°C. More detailed comparison is not possible because the temperatures are different from each other. As shown in Table II, the acid (or neutral) liquids are sorbed a little, while the base liquids are sorbed a lot. Thus, the sorption amount of liquids in PVDF seems to be affected by the acid–base interaction. The higher sorption amount of bases than acids or neutral liquids could be explained more successfully by the acid–base interaction that leads to an exothermic enthalpy change of mixing. The $\Delta 13$ parameter can predict the high amount of sorption of acetone but it cannot explain properly the higher sorption of bases than of acids in PVDF.

Table III shows the sorption selectivities (α_2^1) of binary 50 : 50 mol % mixtures in PVDF and their relations to the difference of $-\Delta H_{1\alpha}$ between component (1) and (2), $\Delta 13/\Delta 23$ [$\Delta 13$ is defined as eq. (3)], and the ratio of molar volumes (V_1/V_2). Sorption selectivity (α_2^1) is defined as the ratio of the molar ratio of liquids (1) and (2) between the polymer and the mixture [$(x_1/x_2)_{\text{polymer}}/(x_1/x_2)_{\text{mixture}}$]. The positive value of $-(\Delta H_{1\alpha} - \Delta H_{2\alpha})$ implies that component (1) interacts more strongly with polymer

(3) than with component (2), so that the positive value of $-(\overline{\Delta H}_{1\alpha} - \overline{\Delta H}_{2\alpha})$ predicts component (1) to be more preferentially sorbed in PVDF over component (2). In the base/cyclohexane binary mixtures, the sorption selectivities increase with the values of $-(\overline{\Delta H}_{1\alpha} - \overline{\Delta H}_{2\alpha})$. In the base/ethanol binary mixtures, the same features are observed, but the values of α_2^1 are less than those of the same base/cyclohexane mixture. In the case that both components of the mixture were electron-donating ones, all of the two could interact with PVDF in a similar strength by acid–base complexation, so that the sorption selectivity would not be high, which is the case for the experimental result for the 1,4-dioxane (1)/ethylacetate (2) system. It should be noted that the ratio $\Delta 13/\Delta 23$, suggested by Lloyd and Meluch[7] to be a preferential sorption indicator, does not provide any good explanation on the high-sorption selectivity of 1,4-dioxane over cyclohexane (or ethanol) in PVDF.

The base (1)/ethanol (2) mixtures show relatively small α_2^1 values than those of base (1)/cyclohexane (2) mixtures, and this seems to be due to the difference of molar volume from liquid to liquid, as suggested by Mulder et al.[8] If the molar volume of a component is smaller than that of the other component, the smaller components would be sorbed preferentially. As shown in Table III, the bases are larger than ethanol but smaller than cyclohexane. Therefore, the bases seem to show the lower sorption selectivities in base/ethanol mixtures than in base/cyclohexane ones.

CONCLUSION

The sorption amount of the base liquid in PVDF was much higher than that of the acid (or neutral) one and the base liquid was preferentially sorbed in the polymer over the acid (or neutral) one. The Fowkes' method was extended to determine the Drago constants of PVDF and the partial molar enthalpy change of mixing at infinite dilution ($\overline{\Delta H}_{1\infty}$) considering acid–base interaction was estimated. It was demonstrated that the sorption amount depends upon the exothermicity of $\overline{\Delta H}_{1\infty}$, while the sorption selectivity is related to the difference $-(\overline{\Delta H}_{1\infty} - \overline{\Delta H}_{2\infty})$. The observations of sorption characteristics for various liquids in PVDF were in good correlation with the present approach considering the acid–base interaction.

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