Colloid Polym Sci 277:687–693 (1999)

SHORT COMMUNICATION

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Solvatochromic studies on the hydrogen-bond donating and dipolarity/polarizability properties of the polyethylene oxide/silica interface

Received: 16 December 1998
Accepted in revised form: 8 January 1999

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Abstract The polarity of the polyethylene oxide(PEO)/silica interface in 1,2-dichloroethane as solvent is classified by means of linear solvation energy (LSE) relationships . The properties of the bare silica particle surface and the silica/PEO interface is expressed by two terms: the dipolarity/polarizability (π^*) of the interface and the hydrogen-bond donating ability (α) of the surface silanols. These terms can be defined by using the Kamlet–Taft solvent parameters α and π^* as a reference system. The interfacial polarity parameters α and π^* were calculated by means of correlation analyses of the energy of the UV/vis absorption maxima of the surface polarity indicators: di-cyano-bis(1,10-phenanthroline) iron II, bis-4,4′-(*N*,*N*-dimethylamino) benzophenone, and 2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate when adsorbed onto the PEO/silica particle surface. The experimental values of the $E_T(30)$ parameter of the PEO/silica interface are compared with independently calculated values employing specific LSE relations derived for well-behaved regular solvents and functionalized silicas. PEO adsorption on silica causes a decrease in the value of the α parameter of the silica surface and an evident increase in the dipolarity/polarizability of the interface.

Key words Solvatochromism – Polyethylenoxide – Silica – Interfacial polarity – Linear solvation energy

Introduction

Adsorption processes of polymers to inorganic substrates are of importance for stabilization of microemulsions and lattices [1]. Polyethylene oxide (PEO) and related polymers when adsorbed to silica have been studied by several authors [2–7]. Adsorption microcalorimetry [3], IR spectroscopy [4], and EPR spectroscopy of labelled PEO chains [7] have been employed to study the intermolecular interactions between PEO chains and the silica surface. The main driving force for the adsorption of PEO chain segments to silica surface groups was attributed to the acid–base interactions of the free electron pairs of the oxygen atoms of the PEO chain [hydrogen-bond accepting (HBA) groups] with the active hydrogen atoms of the silanol groups of the silica surface [hydrogen-bond donating (HBD) groups] (Scheme 1) [2–6]. Of course, dispersion forces and specific interactions between siloxane bridges and the oxygen atoms of the PEO chain are also conceivable [3, 8].

Each of these individual interactions contributes to the measurable overall adsorption energy of PEO chains with the silica surface [3]. The manifold influences upon intermolecular solute/solvent interactions can be expressed advantageously by the linear solvation energy (LSE) relationship of Kamlet and Taft [9–11]. This LSE relationship has also been applied successfully in the quantitative description of adsorption and chromatographic processes at the solid–liquid interface [12–15].

The fundamental Kamlet–Taft approach describes the manifold influence of three polarity terms α, β, and

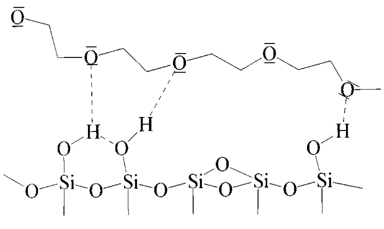
π^* as well as of the Hildebrand solubility parameter (δ_H) on the results of a solvent-dependent chemical process XYZ (Eq. 1) [8–11].

$$\mathrm{XYZ} = (\mathrm{XYZ})_o + h\delta_H^2 + s(\pi^* + d\delta) + a\alpha + b\beta \qquad (1)$$

$(\mathrm{XYZ})_o$ is the value for the solvent reference system, i.e., a nonpolar medium or the gas phase, α is the HBD ability, β is the HBA ability, and π^* the dipolarity/polarizability of the solvents. δ is a polarizability correction term that is 1.0 for aromatic, 0.5 for polyhalogenated, and zero for aliphatic solvents. *a*, *b*, *s*, *h*, and *d* are solvent independent coefficients. They reflect the susceptibility of the solute with respect to these properties.

Polarity studies of the PEO/silica interface within PEO/silica hybrid materials, produced by the sol–gel technique, were reported by Baker et al. [16]. The authors used the fluorescence probe pyrene as the polarity indicator when encapsulated within the hybrid material consisting of PEO and silica. The authors found, surprisingly, that the polarity of the silica/PEO/probe interface was larger than the polarity of the bare silica/probe interface in spite of the established result that the polarity of an interface should to be approximately the average of the polarity of the two contacting phases [17].

However, the use of pyrene as a fluorescence probe to evaluate the polarity of heterogeneous microenvironments has been well established for bare silicas [18], reverse stationary chromatographic phases [14], and composite materials [19]. By using pyrene as a polarity probe, the dipolarity/polarizability of an environment, i.e., that of the PEO/silica interface, is measured by utilizing the intensity ratio Py of the two emission bands I_1 and I_3 at 375 nm and 384 nm, respectively, of the fluorescence spectra of pyrene. Using Eq. (2), Dong and Winnik [20] recommended this Py value, as measured in various solvents as references, as a tool to parameterize the dipolarity/polarizability property π^* of an environment with *n* (set of various solvents) = 32, *r* (correlation coefficient) = 0.959, and the standard deviation (SD) was not reported for this correlation.



Scheme 1 Proposed intermolecular interactions of polyethylene oxide (PEO) segments with silica surface groups. The *dashed lines* indicate possible hydrogen-bond donating (silica)/hydrogen-bond accepting (PEO) interaction sites

$$\mathrm{Py} = 0.64 + 1.33(\pi^* - 0.24\delta) - 0.25\alpha \qquad (2)$$

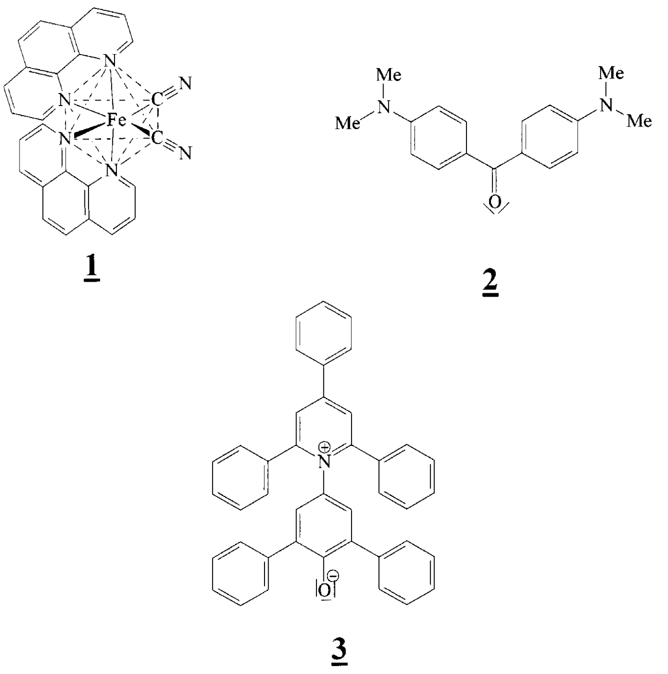
The objective of this paper is the determination of the Kamlet–Taft parameters π^* and α for the PEO/silica interface in a suitable liquid by means of specific solvatochromic dyes. For this study we have selected a specific Aerosil 300 ($\alpha = 1.14$, $\beta = 0.0$, and $\pi^* = 1.00$) [21] as silica powder and a PEO with an average molecular weight of $M_w = 100{,}000\ \mathrm{g\ mol^{-1}}$ and a M_w/M_n ratio of about 2. The values of the Kamlet–Taft parameters for this PEO are $\alpha = 0$, $\beta = 0.65$, and $\pi^* = 0.86$. It is generally expected that the HBD capacity of the silanols decreases after their interaction with a PEO chain because the interaction of the silanol groups with the one electrons of the oxygens of the PEO chain ($\mathrm{HBD_{silica}}$ /$\mathrm{HBA_{PEO}}$ interaction) should dominate. 1,2-Dichloroethane (DCE) ($\alpha = 0$, $\beta = 0.1$, and $\pi^* = 0.81$) was chosen as the solvent for two reasons. PEO is well soluble in this solvent which shows very low HBA and HBD capacity; therefore, HBD/HBA interactions between the silica surface and the solvent are of minor importance. Furthermore, suspensions of Aerosil 300 in this solvent are transparent, which is very convenient for the recording of UV/vis transmission spectra of the adsorbed probe dyes [21–24].

The values of the surface polarity parameters π^* and α are analysed by application of the two carefully characterized solvatochromic dyes $\mathrm{Fe(phen)_2(CN)_2}$ (**1**) and Michler's ketone (**2**) (formular Scheme 2) [22–24]. The solvatochromism of each of these indicators can be well expressed by a LSE relationship according to Eq. (2). $\mathrm{Fe(phen)_2(CN)_2}$ serves as an indicator for the HBD capacity ($a/s = 1.37$), whereas the shift of the UV/v is absorption maximum of Michler's ketone reflects the dipolarity/polarizability ($a/s = 0.81$) of an environment; the coefficients *b* and *d* are zero for both indicators [22].

In two recent papers we have shown that both indicators are well-suited polarity indicators to analyse simultaneously the HBD capacity and the dipolarity/dipolarizability of surface environments, e.g., modified silica particles [21] or cellulose [25].

Values of the $E_T(30)$ polarity parameters of the PEO/silica interface can be measured by means of the well-known Reichardt's dye. The original $E_T(30)$ polarity parameter is defined as the molar absorption energy (ν_{max}) of a specific solvatochromic dye in the respective solvent, namely of 2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate betaine (**3**) (see formular, Scheme 2), expressed in kilocalories per mole (Eq. 3) [26, 27].

The dimensionless E_T^N values are normalized to water as extreme polar ($E_T^N = 1$) and tetramethylsilane (TMS) as extreme nonpolar ($E_T^N = 0$) reference solvents (Eq. 4) [26].



Scheme 2 Formulas of the probe dyes used

$$E_T(30)(\text{kcal mol}^{-1}) = (2.8591)\nu_{\max}10^{-3}(\mathbf{3})(\text{cm}^{-1}) \quad (3)$$

$$\begin{aligned} E_T^N &= E_T^{(\text{solvent})} - E_T^{(\text{TMS})}/E_T^{(\text{water})} - E_T^{(\text{TMS})} \\ &= E_T(30) - 30.7/32.4 \end{aligned} \quad (4)$$

Empirical $E_T(30)$ polarity parameters are well accepted for solvents and various solution processes. Their extension to inorganic particle surfaces has been successfully applied to alumina [28], bare silicas [21, 24, 29], modified silica particles [21, 29], and ormosils [30]. For well-behaved regular solvents, the following LSE equation of the $E_T(30)$ parameter has been calculated by Marcus [31, 32].

$$E_T(30) = 31.2 + 11.5\pi^* + 15.2\alpha \quad (a/s = 1.32) \quad (5)$$

$$n = 166, \quad r = 0.979, \quad \text{SD} = 1.25$$

For functionalized silicas, Spange and Reuter [21] reported a modified LSE relation for the $E_T(30)$ parameter

$$E_T(30)(\text{measured}) = 36.1 + 5.33\pi^* + 14.84\alpha \quad (a/s = 2.7) \quad (6)$$

$$n = 30, \quad r = 0.966, \quad \text{SD} = 1.90$$

Equation (6) suggests that the HBD capacity of the silica surface contributes more strongly to the value of the measured $E_T(30)$ parameter than in well-behaved regular solvents. Both LSE relationships, Eqs. (5) and (6), should be tested independently from each other for their applicability to describe quantitatively the value of the $E_T(30)$ polarity parameter of the PEO/silica interface.

Methods and materials

Materials

$Fe(phen)_2(CN)_2$ **(1)** was prepared according to Schilt [33], Michler's ketone (**2**) was purchased from Merck (Darmstadt) and recrystallized twice from ethanol before use. The probe dye indicator (**3**) was given by C. Reichardt, University of Marburg. PEO was purchased from Fluka. Aerosil 300 was a kind gift from Degussa, Frankfurt am Main. DCE was distilled freshly before use and dried over anhydrous Al_2O_3.

Solvatochromic measurements

The amount of the dyes on the Aerosil surface in DCE was about 1 mg of **1**, 0.1 mg of **2**, and 2 mg of **3**.

For the UV/v is measurements, an MCS 4 diode array spectrometer with glass fibre optics connected with a TSM 5 A immersion cuvette (Carl Zeiss Jena) was used.

Calculation of the polarity parameters

The solvatochromism and properties of these indicators as well as the mathematical procedure for the determination of the individual LSE approaches of the indicators have already been reported in detail [22, 23].

The following multiple correlation equations were used to determine the respective value of the properties α or π^* from the unit of measurement of each $\nu_{\max}$(indicator).

$$\alpha = -7.900 + 0.453\nu_{\max}(\mathbf{1})10^{-3} + 0.021\nu_{\max}(\mathbf{2})10^{-3} \quad (7)$$

$$r = 0.949; \quad \text{SD} = 0.17; n = 34; \quad \text{significance } (F) = 0.000$$

$$\pi^* = 13.889 - 0.251\nu_{\max}(\mathbf{1})10^{-3} - 0.320\nu_{\max}(\mathbf{2})10^{-3} \quad (8)$$

$$r = 0.569; \quad \text{SD} = 0.155; \quad n = 36; \quad F = 0.001$$

The quality of Eq. (7) is really good to examine accurate values of the α parameter. In spite of the poor correlation coefficient of Eq. (8) in calculating π^* values, the significance is sufficient for a determination. This should be considered when interpreting the results.

Results and discussion

Addition of a PEO solution to the silica/probe suspension in DCE causes a remarkable shift of the UV/vis absorption maximum of the adsorbed indicator dyes **1**, **2**, and **3**. The spectral shift of the UV/vis absorption band is time-dependent; however, the equilibrium state of adsorption of PEO to silica is reached almost completely after 5 min. Time-dependent UV/vis spectra are shown in Fig. 1.

Generally, the adsorbed negative solvatochromic indicator dyes **1** and **3** show a bathochromic shift of their UV/vis absorption after addition of PEO indicating that the α and/or π^* values of the surface decrease. In the case of indicator **1**, a shoulder at about 615 nm is

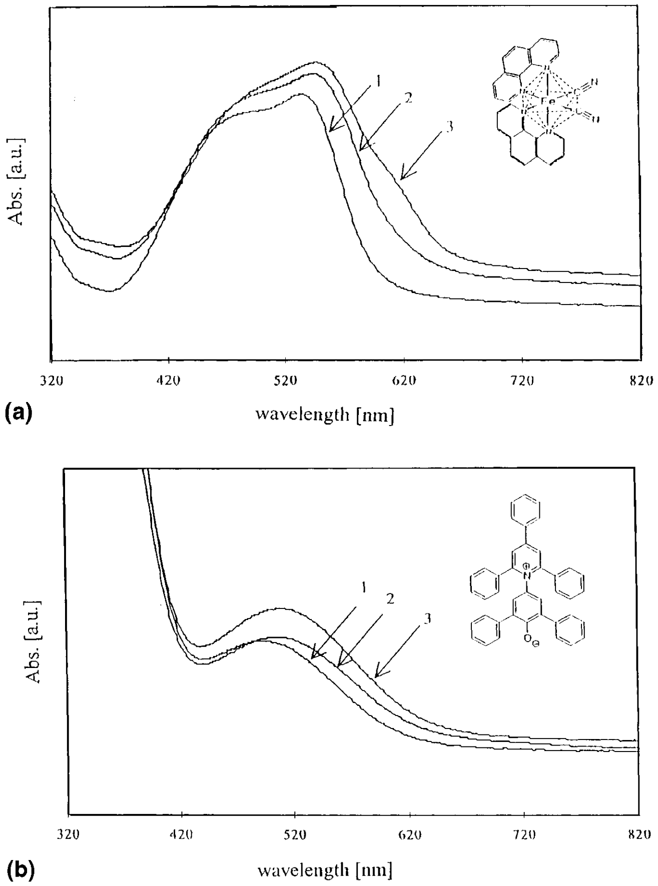


Fig. 1 UV/v is spectra of the polarity indicators **a** **1** and **b** **3** when adsorbed to Aerosil 300 in 1,2-dichloroethane. *1* without polymer, *2* recorded immediately after addition of 30 mg polyethylene oxide (*PEO*), and *3* after 60 min

observed after 60 min adsorption time. This absorption band corresponds to the absorption maximum of **1** in the pure solvent DCE because desorption takes place. The positive solvatochromic indicator **2** shows a bathochromic shift indicating that the α and/or π^* values of the silica surface increase when PEO is adsorbed. The results of the UV/v is spectroscopic measurements and values of the α and π^* parameters calculated using Eqs. (7) and (8), respectively, and the value of the experimentally determined $E_T(30)$ parameters are summarized in Table 1.

The dependencies of values of the α and π^* parameters, respectively, as functions of the adsorption time for the PEO/silica adsorption are shown in Figs. 2 and 3. As expected, the α value of silica decreases after adsorption of PEO due to the moderate $\mathrm{HBD_{silica}}$/$\mathrm{HBA_{PEO}}$ interaction. This result is consistent with zeta potential and solvatochromic measurements of $\mathrm{Fe(phen)_2(CN)_2}$ adsorbed to silica in various HBA solvents [34]: with increasing HBA capacity of the solvent [11, 26], for example, dimethyl formamide (β = 0.69) > tetrahydrofuran (β = 0.55) > acetonitrile (β = 0.4) the extent of the bathochromic shift of the visible absorption of adsorbed $\mathrm{Fe(phen)_2(CN)_2}$ is increased. In this earlier paper [34], we also mentioned that HBA solvents affect the silica surface as a whole and an average polarity was measured. Accordingly, the value of the α parameter of silica also decreases gradually due to functionalization of the silanols with alkyl groups [21].

Adsorption of HBA polymers (PEO with β = 0.65) to silica results in a similar effect on the HBD property of the silica surface as observed by surface functionalization with silane reagents. This effect is only slightly measurable by the visible absorption of the adsorbed phenolate betaine dye **3** because the α value has a weaker contribution to the value of the $E_T(30)$ parameter compared to the influence of the solvent on the UV/v is absorption shift of $\mathrm{Fe(phen)_2(CN)_2}$ [22].

Surprisingly, the value of the π^* parameter of the PEO/silica interface increases considerably with increasing PEO content on the silica surface.

Theoretical values of the $E_T(30)$ parameter were calculated via Eqs. (5) and (6) using the independently examined values of the α and π^* parameters.

It is obvious that the LSE Eq. (5) for the $E_T(30)$ parameter derived for well-behaved regular solvents yields a poorer agreement between experimental and theoretical values of the $E_T(30)$ parameter. Advantageously, the LSE Eq. (6) for the $E_T(30)$ parameter derived for functionalized silicas results in much better agreement between theoretically and experimentally determined values of the $E_T(30)$ parameter. For higher PEO content on the surface, the deviation between measured and calculated values of the $E_T(30)$ parameter also increases; however, this deviation is not dramatic when compared with other complex systems [21, 25]. These good agreements between calculated and measured $E_T(30)$ values evidently support both the correctness of our data and the specific LSE correlation for the values of the $E_T(30)$ parameter for functionalized silicas. This conclusion is, therefore, of importance because of the low correlation coefficient for the multiple correlation Eq. (8) for determining the value of the π^* parameter. Thus, it seems that both Eqs. (7) and (8) are useful for this purpose.

Generally, we found that the dipolarity/polarizability of the silica PEO/DCE interface is larger than that of the silica/DCE interface. As already mentioned, this result is consistent with the independently observed result for the PEO/silica interface of a hybrid material synthesized by the sol–gel technique [16].

In Ref. [21] we reported that the α value is a function of the surface coverage Γ which is the surface coverage of silica with alkyl groups expressed in micromoles per metre squared of silica [21] (Eq. 9).

Table 1 Measured UV/v is absorption maxima of the indicator dyes **1**, **2**, and **3** when adsorbed to 300 mg Aerosil 300 in 25 ml 1,2-dichloroethane and after adsorption of polyethylene oxide (*PEO*) (added as a solution in $CHCl_3$) and calculated α, π^*, and $E_T(30)$ values

Time (min)	$\nu_{max}(\mathbf{1})$ $10^3/cm^{-1}$	$\nu_{max}(\mathbf{2})$ $10^3/cm^{-1}$	$\nu_{max}(\mathbf{3})$ $10^3/cm^{-1}$	α	π^*	$E_T(30)$ Eq. (3) (measured)	$E_T(30)$ Eq. (5) (calculated)	$E_T(30)$ Eq. (6) (calculated)
	18.80	25.51	20.20	1.14	1.00	57.8	60.0	58.3
15 mg PEO								
0	18.35	25.19	19.80	0.93	1.22	56.6	59.3	56.4
0.5	18.32	25.00	19.72	0.92	1.28	56.4	59.9	56.6
1	18.32	25.00	19.69	0.91	1.28	56.3	59.8	56.4
3	18.32	24.94	19.69	0.91	1.30	56.3	60.0	56.5
5	18.32	24.94	19.69	0.91	1.30	56.3	60.0	56.5
10	18.32	24.88	19.65	0.91	1.32	56.2	60.2	56.6
30	18.32	24.88	19.65	0.91	1.32	56.2	60.2	56.6
60	18.32	24.85	19.65	0.91	1.32	56.2	60.2	56.6
30 mg PEO								
0	18.35	25.00	19.61	0.92	1.28	56.1	59.9	56.6
0.5	18.30	24.75	19.50	0.90	1.36	55.7	60.6	56.7
1	18.25	24.39	19.46	0.87	1.50	55.6	61.6	57.0
3	18.25	24.26	19.46	0.86	1.54	55.6	62.0	57.1
5	18.21	24.15	19.46	0.85	1.58	55.6	62.2	57.1
10	18.21	24.00	19.38	0.84	1.64	55.4	62.8	57.3
30	18.21	23.97	19.38	0.84	1.64	55.4	62.8	57.3
60	18.20	23.87	19.38	0.84	1.66	55.4	63.0	57.4
60 mg PEO								
0	18.28	24.75	19.23	0.89	1.37	55.0	60.5	56.6
0.5	18.25	24.57	19.19	0.87	1.44	54.9	61.0	56.7
1	18.25	24.51	19.19	0.87	1.46	54.9	61.2	56.6
3	18.25	24.27	[a]	0.86	1.54	–	62.0	57.1
5	18.21	24.15	[a]	0.85	1.58	–	62.2	57.1
10	18.18	24.10	[a]	0.83	1.61	–	62.3	56.9
30	18.15	24.10	[a]	0.81	1.62	–	62.2	56.7
60	18.15	24.10	[a]	0.81	1.62	–	62.2	56.7

[a] The interface polarity is not measurable because dye **3** desorbs from the particle surface

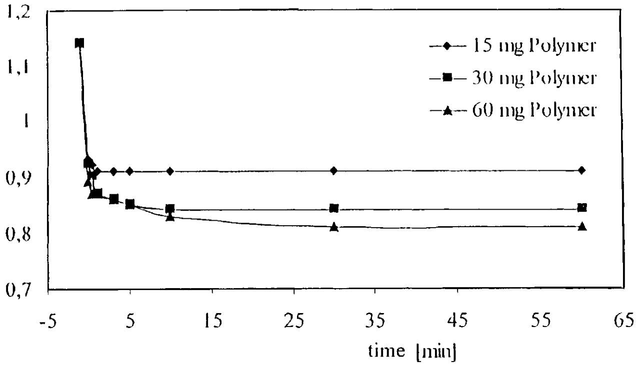


Fig. 2 Decrease in the value of the Kamlet–Taft α term of Aerosil 300 with adsorption time of PEO depending on the amount of PEO added

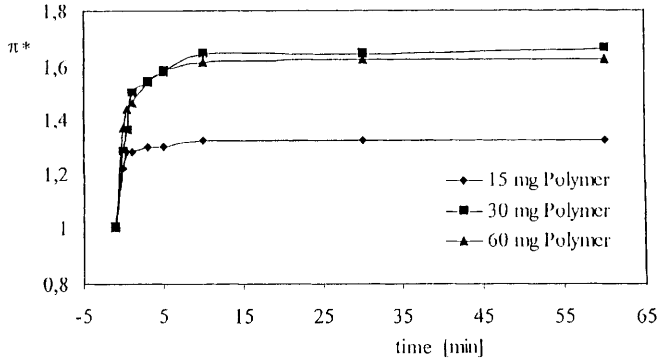


Fig. 3 Increase in the value of the Kamlet–Taft π^* term of the Aerosil 300 PEO interface with adsorption time of PEO depending on the amount of PEO added

$$\alpha = 1.137 - 0.113\Gamma \qquad (9)$$

$$r = 0.991;\ SD = 0.228$$

Using the α value from Table 1 for 60 mg PEO/300 mg Aerosil, it is assumed that 30% of the silanols can actually be covered by PEO chains in DCE solution. The indicator **2** is also located within the polymer/silica layer because in the surrounding DCE solution the typical absorption of **2** should appear at $\nu_{max} = 28200\,cm^{-1}$. The strong bathochromic shifts of **2** successively increase with adsorption time. This shows that the values of the π^* parameter of solid/solid [14, 16] as well as of solid/

liquid interfaces [13, 21] are influenced in a very complex manner. Probably the π^* indicator is influenced by co-operative interactions by both PEO and silica components [22].

The results reported in this work do, however, also raise the following question: is the increase in the dipolarity/polarizability of the interface of an acidic surface after polymer adsorption (interaction or incorporation) a specific result of PEO/silica interaction or is it a general phenomenon? Therefore, we will briefly report on recent results of solvatochromism of two other polymer/silica compositions, namely for the adsorption of polyvinylamine (PVAM) on silica in water and of polyvinylpyridine on silica in DCE. The solvatochromic measurements of the solid PVAM/silica adsorbates were also carried out in DCE; however, the PVAM was adsorbed to silica from an aqueous solution in a previous step because this polymer is insoluble in common organic solvents. After separation and drying the sample in vacuo at room temperature, it was treated with the probe dyes as for the PEO/Aerosil adsorption measurements. However, residual water is included by employing this procedure for the PVAM/silica samples.

The solvatochromic results of both compositions point in the same direction as the results of PEO/silica adsorption: adsorption of a polymer on an acidic silica surface causes an increase of the interfacial dipolarity/polarizability and a decrease in the HBD capacity of the acidic surface.

Conclusion

The results show that solvatochromism of well-suited surface polarity indicators can be used for characterization of the surface as well as of the interfacial polarity of the polymer/solid interaction.

The applicability of LSE correlations derived for functionalized silicas is also suitable for polymer/silica adsorbates in analysing polarity measurements of solid materials by solvatochromic dyes. It is expected that the concept employed can be extended to other polymer/solid surface interactions. By applying Eq. (2) and the data from Ref. [16], the agreement of the results between the different indicators is very promising for the establishment of a common method for measuring the interface polarity of hybrid and composite materials. The important question remains: at which site is the probe dye located within the polymer/silica interface? Generally, a probe should be localized at the site which corresponds to the minimum of the free energy.

Acknowledgements Financial support for this project in particular by the DFG, the Fonds der Chemischen Industrie, and BASF Aktiengesellschaft is gratefully acknowledged.

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