Component Interactions and the Stability of Some Pigment/Polymer Dispersions

P. MUKHOPADHYAY,[1] L. DESBAUMES,[1] H. P. SCHREIBER,[1] AH-MEE HOR,[2] G. DIPAOLA-BARANYI[2]

[1] Department of Chemical Engineering, École Polytechnique, P.O. Box 6079, Stn. Centre-Ville, Montreal, Quebec H3C 3A7, Canada

[2] Xerox Research Center of Canada, 2660 Speakman Drive, Mississauga, Ontario L5K 2L1, Canada

ABSTRACT: The sedimentation behavior of rutile and selected organic pigments dispersed in polymer solutions has been interpreted in terms of acid–base interactions at the polymer/pigment interface. The acid–base information was obtained from inverse gas chromatography. Moderate strengths of acid–base interaction were beneficial to the stability of dispersions, whereas both the absence of and excessive interaction resulted in the rapid deposition of solids. The effect is associated with the orientation of adsorbed polymer molecules, which must provide an adequate steric (entropic) barrier for the aggregation and deposition of solids. Implicated is the balance of interaction forces at pigment/polymer and polymer/solvent contacts. Rheological data for the dispersions have been used to obtain a parameter related to the thickness of the adsorbed polymer layer, by way of amplifying on the state of the pigment/polymer interface. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 245–253, 1998

Key words: dispersion; pigments; polymer solutions; acid–base interactions; dispersion rheology; polymer adsorption; inverse gas chromatography

INTRODUCTION

Dispersions of pigments in polymer solutions are of prime importance to several industries. The ease of dispersing solids in organic vehicles and the stability of ensuing dispersions are of concern in the formulation of protective coatings. Similar concerns exist in manufacturing organic photoconductors, wherein dispersion stability is an important factor in the selection of both photogenerator pigments and polymer vehicles. Generally, in nonaqueous systems, the stability of dispersed solids is dependent on the adsorption of polymer chains, which act as entropic barriers for the coalescence and eventual sedimentation of dis-

persed particles.[1,2] Polymer adsorption onto the surfaces of pigments is driven by thermodynamic forces. The surface energies of pigments, particularly inorganic ones, tend to be much greater than those of polymers, a factor favoring the anchoring of polymer chains at high-energy sites of the solid. The balance of specific interactions also plays an important role, as shown by the work of Fowkes[3] and Tiburcio and Manson.[4] These workers reported that the quantity of adsorbed polymer and its orientation depend on interactions at polymer/solid and polymer/solvent contacts. For convenience, Fowkes[3,5] adopted the convention of labeling all nondispersive force interactions as acid–base interactions and used Drago's (Lewis) acid–base theory to rationalize the adsorption behavior of some polymer/particulate combinations.

Analogous lines of argument have been followed in recent work from these laboratories. Stressed in our approach has been the use of in-

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verse gas chromatography (IGC)[6] to determine acid−base interaction constants for polymers and pigments. For this purpose, use is made of Gutmann's[7] theory of Lewis acids and bases, and protocols reported by Saint-Flour and Papirer[8] and Schultz and Lavielle.[9] Interaction criteria have been established for pigments and polymers, and these proved to be useful in interpreting aspects of dispersion behavior[10] and the rheology of pigment dispersions in polymer solutions.[11]

This article is directed at the behavior of pigment dispersions in polymer solutions relevant to photoconductors. The stability of dispersions has been examined in light of interaction criteria, again obtained from IGC, with rheological data used to elaborate on the state of polymer molecules adsorbed on surfaces of the selected pigments.

EXPERIMENTAL

Materials

The polymer vehicles used in this work were a bisphenol polycarbonate (PCZ), a styrene-4-vinyl pyridine block copolymer (SVP), and a poly-(vinyl butyral) (PVB). PCZ, a 4,4′-cyclohexylidenebisphenol polycarbonate, was obtained from Mitsubishi Gas Co. (Nagoya, Japan) and described earlier by DiPaola-Baranyi and coworkers.[12] Gel permeation chromatography (GPC) evaluations (Varian 5000 LC apparatus) showed it to have $Mw = 170,000$ and $Mn = 67,000$. The SVP, supplied by the Xerox Research Center of Canada (Missisauga, Ontario, Canada), had a block length ratio S : VP = 480 : 79, with the styrene $Mn = 50,000$ and a polydispersity < 1.1. The PVB, obtained from Aldrich Chemicals (Milwaukee, WI), had a 70 mol % butyral, 25 mol % hydroxy, and 5 mol % acetyl content.[13] All three of the polymers were used in solutions, with redistilled cyclohexanone (CHX) as solvent. Reagent-grade toluene (TO) was used as an alternative solvent for PCZ, and butyl acetate (BuAc) was used as an alternative for SVP.

Pigments included an inorganic rutile (R) supplied by Tioxide Canada. It bore a combined organic/inorganic surface coating, applied by the manufacturer. Brunauer−Emmet−Teller (BET) determinations indicated a specific surface area of 9.7 m^2/g. Three organic pigments were included in this study. These were a benzimidazole perylene (BP), a titanyl phthalocyanine (coded PHA),

and a hydroxy gallium PHA (PHB). The organic pigments had similar surface areas near 95 m^2/g. Pigment densities were determined as 4.1 g/mL for rutile and 1.6 g/mL for each of the organic solids.

Procedures

The following data summarize the various experimental procedures exacted by the program.

Dispersion/Sedimentation

Polymer solutions used as vehicles for pigment dispersions were prepared along the lines discussed previously.[11] Briefly, 0.75 g of polymer was dissolved in 48 mL of solvent. The solution was placed in a 150 mL porcelain jar and to this was added a 0.75 g pigment and 300 g of 0.30 cm stainless-steel balls. The stoppered jar was placed on a two roll mill. This was operated at 45 rpm for a 24-h period, wherein the pigment dispersion was decanted, and the steel grinding media recovered and prepared for reuse. Dispersion samples were placed in graduated 10-mL centrifuge tubes, and the volume of sedimented pigment was recorded for periods of up to 1,000 h. Finally, tubes were centrifuged for 60 min to obtain final values of sedimented pigment volumes. All of these steps were conducted in duplicate. Quoted values of sedimentation rates and volumes are reproducible to ±5%.

IGC

Different procedures were followed in preparing polymer and pigment stationary phases for IGC measurements. Polymers were dissolved in CHX and then contacted with Chromosorb AW support. Polymer deposition on the support was by slow evaporation in Rotovap apparatus. Standard ashing procedures[14] indicated that the mass of deposited polymer in each case fell in the range of 7−9 wt %, considered to be well suited for IGC analyses.[6] Coated support was packed in previously degreased and washed 0.7 cm. o.d. stainless-steel columns, typically 80−130 cm. in length. Pigments were deposited directly into stainless-steel tubes 1.5 cm o.d. and 25 cm long. The mass of pigment in the columns varied with their specific surface areas to make available roughly equivalent amounts of surface. In the case of rutile, 2.68 g of the material offered a total surface area of 26 m^2. The BP column contained 0.26 g of pigment equaling 24.8 m^2, and the total surface areas for

PHA and PHB were 24.4 and 25.9 m^2, respectively.

Columns were placed in a Varian 3400 chromatograph equipped with both heated wire and flame ionization detectors. Helium was the carrier gas, and all columns were conditioned for 24 h at 160°C under a flow of the gas. All IGC determinations were made in the 30–60°C temperature range. Retention volumes were obtained for volatile probes including the n-alkanes from C_6 to C_{10} and for benzene, chloroform, tetrahydrofuran, diethylether, and acetone. According to Gutmann's[7] classification, the first two of these represented Lewis acids, the next two Lewis bases, and acetone the amphipatic category. Vapors were injected at infinite dilution from 10-μL Hamilton microsyringes. Carrier gas flow rate was held at 12 mL/min, consistent with the generation of symmetric elution peaks that were found to be independent of the flow rate in the 6–15 mL/min range. Retention times were measured in triplicate, with a repeatability of better than 4%.

The emphasis in IGC work was on the evaluation of thermodynamic interactions between pigments and polymers and between polymers and solvents. Pigment/polymer interactions were characterized by acid–base interaction potentials, Ka and Kb. These were obtained by following protocols fully described in the recent literature.[8,9,15] Required is the generation of a reference line linking the retention volume Vn of alkanes with the liquid state surface free energy of these vapors by

$$RT \ln Vn = 2Na(\gamma_1^d)^{1/2}(\gamma_s^d)^{1/2} + C \quad (1)$$

Here, a is the cross-sectional area of the adsorbed molecule (values given by Schultz and Lavielle[9] were used in this work), the γ's are dispersion contributions to the surface free energy of vapor and solid, N is Avogadro's number, C is an integration constant, and R and T have their usual meaning. When solids can interact with vapors through acid–base forces, then injected polar probes will fall off the reference line generated by plotting the left-hand side of eq. (1) versus $a(\gamma_1^d)^{1/2}$, thereby defining the acid–base contribution to the free energy of vapor adsorption, ΔG_{ab}, from

$$\Delta G_{ab} = RT \ln \frac{Vn}{(Vn)_{\text{ref}}} \quad (2)$$

where Vn is the retention volume of the polar probe and $(Vn)_{\text{ref}}$ is the corresponding datum for an alkane vapor with the same dimension. Following Saint-Flour and Papirer[8] and Schultz and Lavielle,[9] the free energy datum is determined over an appropriate T range, leading to the calculation of the enthalpy term, ΔH_{ab}. This is then used to evaluate Ka and Kb from the equation

$$\frac{\Delta H_{ab}}{AN^+} = Ka \frac{DN}{AN^+} + Kb \quad (3)$$

where AN^* and DN are (known) Gutmann acceptor (acid) and donor (base) numbers for the vapors used in the determination, with the former corrected by the method of Riddle and Fowkes[16] to achieve consistency in the units for these characterization parameters.

Polymer/solvent interactions were represented by the Flory–Huggins χ. For this purpose, the vapors of solvents used in this work were injected into the polymer columns, again at infinite dilution and at $T = 30$°C.* The specific retention volumes were then used to obtain χ after Deshpande and coworkers[17] and Su and associates[18]:

$$\chi_{1,2} = \ln[273.2Rv_2/Vnp_1^\circ V_1] - [1$$
$$- V_1/V_2]\phi_2 - p_1^\circ[B_{11} - V_1]/RT \quad (4)$$

Here, subscripts 1 and 2 refer to the vapor and polymer phases, respectively; v_2, V_2, and ϕ_2 are the specific volume, molar volume and polymer volume fraction, respectively; and V_1 and p_1° are the molar volume and saturation vapor pressure of the volatile phase. B_{11} is the second virial coefficient used to correct for nonideality in the vapor phase and calculated from corresponding equations of state.[19]

Dispersion Rheology

A Bohlin VOR Rheometer was used for rheological measurements on pigment dispersions and unpigmented polymer solutions. Data accumulation was restricted to the combinations PCZ/R and

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*Strictly, eq. (4) is to be applied at temperatures above the T_g of the stationary phase to evaluate the interaction between bulk polymer and solvent. In this work, as on other occasions,[11] interest is focused on interactions at polymer surfaces. Determinations conducted well below the polymer, T_g, as in the present instance, restrict the significance of data to the polymer surface region. The χ values reported herein, therefore, are correspondingly restricted and will not necessarily equal χ evaluated at $T > T_g$.
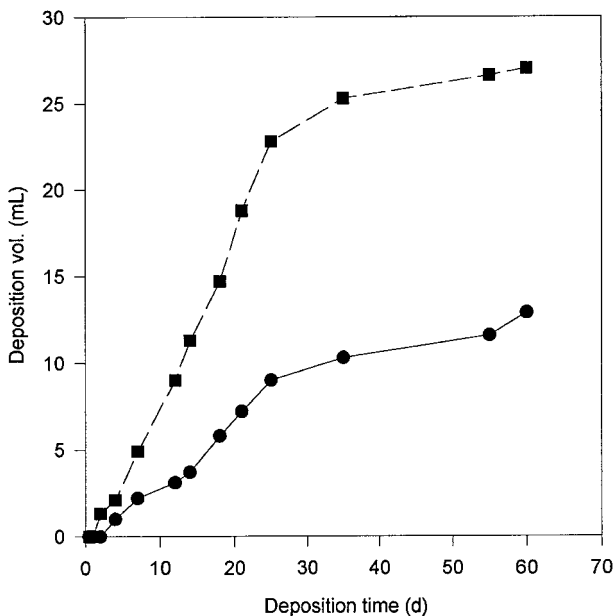
Figure 1 Sedimentation rates for PHB pigment from CHX solutions of polymers: (●) PVB; (■) SVP.

PCZ/PHB and to the SVP combination with PHB and BP as the adsorbing solids. Measurements were made on dispersions prepared (as described) for sedimentation. For the present purpose, however, three levels of pigmentation were studied. These were at pigment volume fractions of 0.13, 0.27, and 0.35. Steady-state shear responses were measured over 3 decades of shear, in both increasing and decreasing shear modes. Data were found to be independent of the direction of shear rate variation. Throughout, the temperature was 25°C.

RESULTS AND DISCUSSION

Wide variations were observed in the stability of pigment dispersions. For any given pigment, the selection of stabilizing polymer exerted considerable influence. This is illustrated in Figure 1, showing the deposition paths of PHB pigment when dispersed in CHX solutions of PVB and SVP. Whereas both polymers confer appreciable short-term stability to the pigment dispersion, SVP ultimately is less effective, allowing a considerably greater volume of pigment to deposit in a 60-day period than is the case with PVB as the stabilizer. Variations also were observed in the efficacy of any one polymer as a stabilizing medium for the solids used in this work. Finally, the selection of solvent also impacted on the results

(as shown in Fig. 2). This compares the deposition paths of pigment PHA from solutions of polymer PCZ in CHX and TO. Clearly, TO is a less favorable solvent medium. Presumably polymer–solvent interactions in this case are either too strong to favor the adsorption of the polymer, or too weak, thus leading to a polymer conformation in the adsorbed state that is unfavorable for the formation of an effective steric barrier.[1,2]

Notable in Figure 2 is the attainment of an equilibrium value of sedimentation volume for the TO solution case, and, in Figure 1, the near-equilibrium when SVP is the stabilizing macromolecule. In these cases, it is apparent that a convenient parameter may be defined to compare the performance of different dispersion systems. The parameter chosen is $t_{1/2}$, the time required to attain 50% of the ultimate volume of sedimented solids. The ultimate volumes were obtained by centrifuging the dispersions, as noted earlier. Values of the $t_{1/2}$ parameter have been entered in Table I. They will be used later in this article to rationalize pigment deposition processes.

The significant dependence of dispersion stability on the choice of solvents and polymers suggests the importance of component interactions. IGC experiments were used to provide quantitative indexes of interaction, as noted in the previous section. Excellent linear relationships, conforming to the stipulate of eq. (1), were obtained for each of the polymer and pigment stationary phases. This
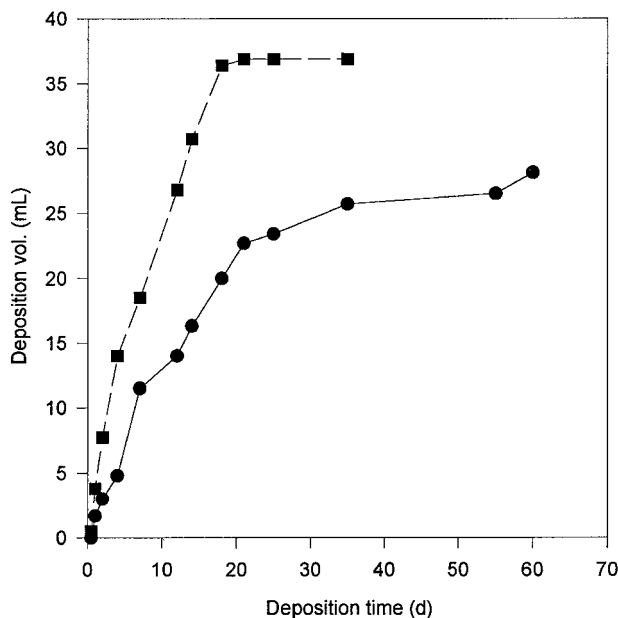

Figure 2 Sedimentation rates for PHA pigment from solutions of PCZ in (●) CHX and (■) TO.

Table I Summary of Sedimentation Time Parameters

	$t_{1/2}$ (d) in		
System	CHX	TO	BuAc
PCZ/R	2.5	7.5	—
PCZ/BP	4.5	12.0	—
PCZ/PHA	32	27	—
PCZ/PHB	13.5	17.0	—
PVB/R	9.5	—	—
PVB/BP	11.5	—	—
PVB/PHA	21	—	—
PVB/PHB	24	—	—
SVP/R	3.5	—	5.0
SVP/BP	8.5	—	4.0
SVP/PHA	41	—	37
SVP/PHB	31	—	21

resulted in the evaluation of acid–base interaction numbers (summarized in Table II). Also listed are values of γ_s^d. The dispersion surface-free energies of the pigments exceed those of the polymers, so that in all polymer/pigment combinations, dispersion forces will favor polymer adsorption. The effect should be particularly noted when rutile is the adsorbent. The acid–base parameters identify PVB and BP as net acids, PCZ SVP and rutile as net bases, and PHA and PHE pigments as weakly interacting, amphipatic solids. Noteworthy is the dependence of Ka and Kb for PCZ and SVP on the choice of solvent. Many polymers have the ability to undergo surface restructuring[20] in response to the orienting power of the medium in contact with them. The effect has been documented elsewhere for a series of SVP diblock polymers.[21,22] Evidently, both PCZ and the present SVP copolymer may restructure and display different surface compositions and/or orientations when recovered from the indicated solvents. Regardless of solvent, however, in combinations such as PCZ/BP and PVB/R, the dispersion stabilities may be strongly influenced by acid–base interactions. On the other hand, in acid–acid or base–base pairs (such as PVB/BP or SVP/R), the contribution of acid–base interactions should be much less pronounced. A quantitative index of component pair interactions is needed and presented in the form of Isp, empirically defined[23] as

$$Isp = (Ka)_1(Kb)_2 + (Ka)_2(Kb)_1$$
$$- (Ka)_1(Ka)_2 - (Kb)_1(Kb)_2 \quad (5)$$

where subscripts 1 and 2 denote polymer and pigment. Data are presented in Table III. The table also lists χ values for the polymer–solvent combinations of this work.

The Isp parameters indicate strong interactions between BP and each of the polymers, and much milder acid–base effects involving PHA and PHB. Particularly interesting is the rutile case, in which appreciable acid–base interaction may be expected with PVB as the stabilizing moiety, but none when PCZ or SVP are involved. An examination of Isp and relevant χ suggests that polymer partitioning between solvent and particulate surface may well be affected by the choice of solvent. For example, PCZ might be expected to adsorb more massively out of TO than out of CHX, with which it is somewhat more miscible. Of course, the mass of polymer adsorbed on the solid is not necessarily a sufficient criterion of dispersion stability; the conformation of adsorbed chains may play an important part in the stability of pigment dispersions.

A test of the significance of acid–base interactions is their relation to the observed $t_{1/2}$ values in Table I. This is represented in Figure 3. The relationship, although complex, is significant. Dispersion stability is impaired by both the absence of acid–base interactions (denoted by $Isp < 0$) and by excessive specific interactions (denoted by $Isp \geq 5$). This would seem to relate to the conformation of the adsorbed chain. In the absence of acid–base forces, only weak dispersion forces promote the adsorption of polymer chains. These, therefore, are likely to be weakly anchored, major portions of the chain remaining in an extended state in the solvent medium. Under these conditions, close approach of pigment particles

Table II Acid–Base and Dispersion Surface-Free Energy Data for Materials of This Work

Material	Ka		Kb		γ_s^d (mJ/m^2)
PCZ	5.7[a]	4.4[b]	10.1[a]	6.0[b]	22.8
SVP	3.0[a]	2.7[c]	5.5[a]	7.5[c]	32.7
PVB	5.1[a]		3.8[a]		31.5
R	4.6		7.8		46.0
BP	6.7		3.4		38.4
PHA	2.7		2.3		36.7
PHB	1.4		1.9		35.8

[a] In CHX.
[b] In TO.
[c] In BuAc.

Table III   Summary of Acid–Base and Thermodynamic Interaction Parameters

Pigment Interactant	Isp for					
	PCZ		PVB		SVP	
R	-13.6^a	-5.0^b	4.1^a		-17.7^a	-15.3^c
BP	14.6	5.2	-4.2		8.3	15.8
PHA	1.8	1.0	-0.4		1.1	2.0
PHB	-2.2	-0.8	0.6		-1.2	-2.4

χ for				
PCZ/CHX	PCZ/TO	PVB/CHX	SVP/CHX	SVP/BuAc
0.16	0.35	0.03	-0.14	-0.38

[a] Denotes CHX.
[b] Denotes TO.
[c] Denotes BuAc.

may result in the entanglement of adsorbed chains and the consequent formation of agglomerates that sediment rapidly. At the other extreme of excessive interactions, adsorbed chains may be tightly bound to the pigment surface, providing little hindrance to the collision and agglomeration of solid particles. This again would result in the
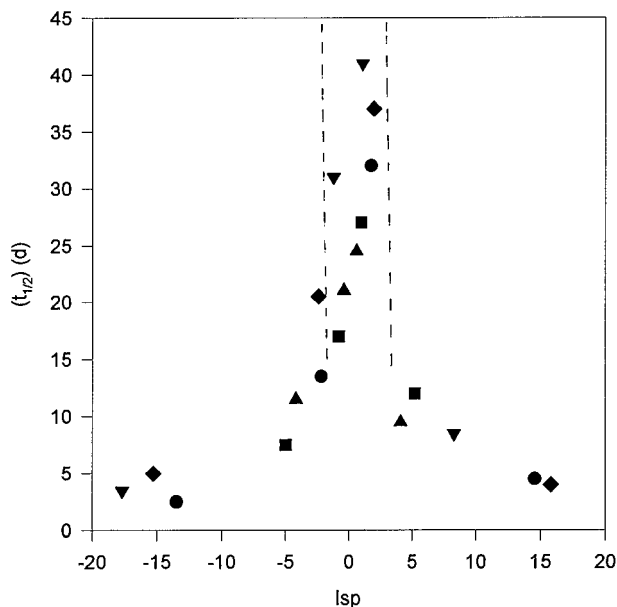

Figure 3 Relationship between pigment sedimentation parameter and polymer/pigment acid–base pair interaction. (●) PCZ in CHX; (■) PCZ in TO; (▲) PVB in CHX; (▼) SVP in CHX; (◆) SVP in BuAc.

rapid deposition of dispersed solids. At moderate values of Isp, where a reasonable balance exists between polymer/solvent and polymer/pigment interactions, the polymer may be assumed to anchor repeatedly on the solid surface, whereas still extending nonadsorbed moieties into the solvent. Entropic (steric) stabilization[1,2] would result from this conformation. Accordingly, in the systems under consideration, preferred values of Isp should lie in a narrow range centered on $Isp \approx 2$. The adsorption/solvation principles advanced herein should lead to varying thicknesses of adsorbed polymer layers. In principle, this is open to experimental examination by rheological data discussed herein.

The viscosity versus shear rate data obtained for the present systems are illustrated in Figure 4. This shows the viscosities of an unpigmented CHX solution of PCZ and the corresponding dispersion, with R as the solid at a volume fraction $\Phi = 0.27$. As in all other cases, the viscosity of the unpigmented polymer solution is Newtonian. At the selected pigment load, the dispersions were found to be mildly shear-thinning, a trend well illustrated in Figure 4. The primary interest here is the relationship between the relative viscosity, $\acute{\eta}$ and the pigment volume fraction, Φ, where $\acute{\eta}$ is the ratio of the dispersion viscosity to that of the corresponding polymer solution, at a reference rate of shear. The reference was taken as $\acute{\eta}$ at infinite shear, computed from the Casson equation,[24] which very well fitted experimental data.
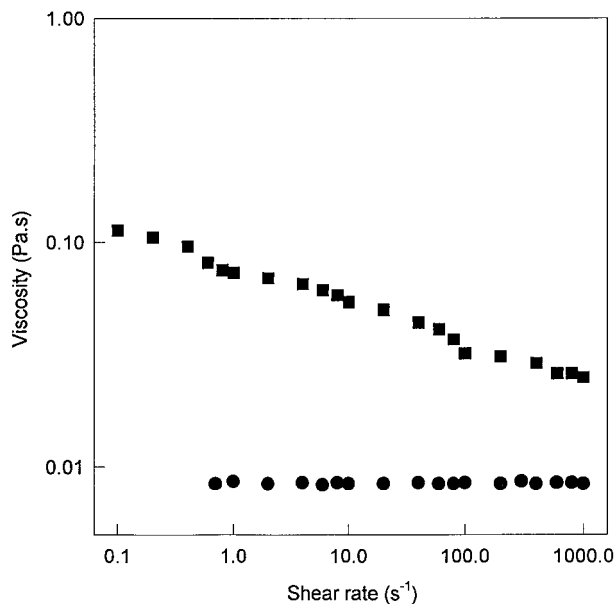
Figure 4 Viscosity-shear rate data (25°C): (●) unpigmented solution of PCZ in CHX; (■) same polymer vehicle with 0.27 volume fraction of R pigment.

Many expressions have been proposed to relate $\dot{\eta}$ with Φ. One of the more successful of these is the Maron–Pierce equation,[25] written as

$$\dot{\eta} = (1 - \Phi/\Phi_m)^{-2} \qquad (6)$$

where Φ_m is the maximum packing fraction of the solid. As in an earlier study,[11] we have chosen the value of 0.63 that falls midway between simple cubic and tetrahedral packing of the pigment particles. Not surprisingly, however, in no case was there agreement between calculated and experimental values of $\dot{\eta}$, because any adsorption of polymer on the available pigment surface would change pigment dimensions. Thus, there is a difference between the apparent pigment volume fraction, as computed from the composition of the system, and the effective value, Φ_e, following polymer adsorption. Accordingly, we rewrite eq. (6) in the form

$$(\dot{\eta}_r)^{-1/2} = 1 - f(\Phi/\Phi_m) \qquad (7)$$

the correction factor f being tantamount to a measure of the change in pigment particle dimension and thus related to the thickness of the adsorbed layer. Expectedly, f would be a function of Isp and may also vary with χ.

Table IV presents a summary of experimental relative viscosities and values for the correction factor, f. In all cases, $f > 1.0$, although the parameter is a decreasing function of pigment concentration, coming close to unity at the highest pigment volume fraction. In good measure, this is an artefact of the limited quantity of available polymer, leaving portions of the solid surface covered (wetted) only by solvent molecules. The f values at $\Phi = 0.13$ seem reasonable as a basis for comparison. These range from near unity to >1.8. A large variation of adsorbed layer thicknesses and, consequently, in mass and orientation of adsorbed polymer molecules, may be postulated. Reference to Table III also makes evident an effect of solvent choice. In PCZ solutions, use of the thermodynamically stronger solvent, CHX, results in lower values of f than when TO is the solvent. Presumably, the solvent competes excessively for PCZ, leaving the pigment surfaces only partially protected by adsorbed PCZ, and reducing the net layer thickness. The results for SVP solutions are intriguing. Both solvents of this polymer are thermodynamically "good," but in SVP/BP the f value is greater when the stronger solvent is used, whereas with PHB as the pigment, the situation is reversed. Evidently, complex relationships may be expected between f, χ, and the pair interaction value Isp. Analogously, the relationship involving the dispersion stability parameter, $t_{1/2}$, Isp, and χ also would be complex.

A test of expectations is found in Figure 5, where f is shown as a function of Isp. Data suggest a broad envelope of behavior, with the thickness factor f generally rising with Isp. An increase in the layer thickness with increasing acid–base interaction at pigment/polymer contacts is intuitively reasonable. The complexity of the shown relation, however, reflects on the omission from consideration of functional dependencies between f and χ, alluded to previously, between Isp and χ and contributions to the mass and conformation of adsorbed polymer arising from dispersion forces. Neglect of possible variations in pigment/solvent interactions further confines the correlation in Figure 5 to semiquantitative status. An attempt to relate Isp, χ, and $t_{1/2}$ would call for three-dimensional representation. Unfortunately, the number of data points available is not sufficient to generate a meaningful solid surface. This remains an objective for future studies.

CONCLUSIONS

The combination of experimental data from IGC and steady-state rheological procedures has been

Table IV   Data from Rheological Investigation of Pigment Dispersions

	Φ/Φ_m:	0.206		0.429		0.555	
	$(\eta)^r_{calc}$:	1.59		3.07		5.05	
		$(\eta)^r_{ex}$	f	$(\eta)^r_{ex}$	f	$(\eta)^r_{ex}$	f
PCZ/R[a]		1.81	1.25	3.41	1.07	5.63	1.04
PCZ/R[b]		2.07	1.48	3.93	1.16	6.64	1.10
PCZ/PHB[a]		2.01	1.43	3.77	1.13	5.90	1.06
PCZ/PHB[b]		2.40	1.72	4.18	1.22	7.07	1.13
SVP/BP[a]		2.14	1.54	3.90	1.15	5.50	1.03
SVP/BP[c]		2.51	1.83	4.27	1.21	6.21	1.08
SVP/PHB[a]		1.96	1.39	3.64	1.11	5.70	1.05
SVP/PHB[c]		1.62	1.05	3.12	1.01	5.16	1.01

[a] Denotes CHX.
[b] Denotes TO.
[c] Denotes BuAc.

used to examine the stability of pigment dispersions in nonaqueous solutions of PCZ, SVP, and PVB polymers.

The stability of dispersions of inorganic and organic pigments has been related to the acid−base interaction at the polymer/pigment interface. A range of interaction values has been identified that favor dispersion stability.
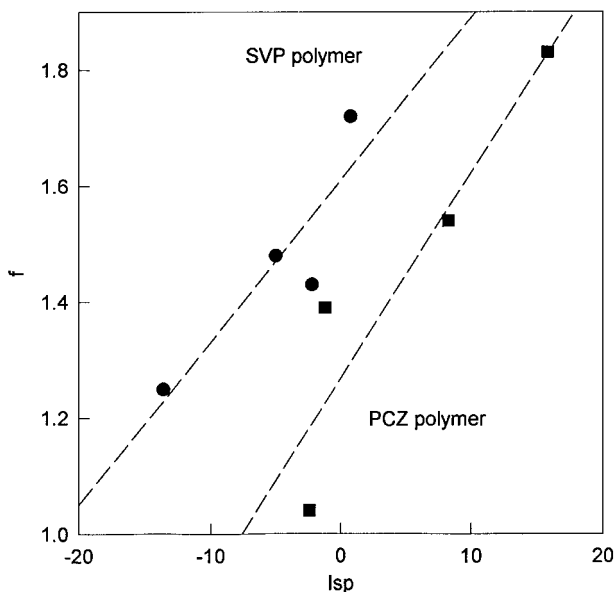
Acid−base interaction criteria, although essential to the stabilization process, are insufficient to account for all observations. Reasons advanced are that dispersion stability is related to the adsorption of polymers from solution onto pigment surfaces, and their conformation in the adsorbed state. These factors, in addition to depending on acid−base considerations, also depend on thermodynamic interactions between polymer and solvent and between pigment and solvent. Additional contributions are postulated to arise from dispersive forces acting at the diverse interfaces of a dispersion. Quantitative representation of these contributions will be required fully to rationalize dispersion and stabilization processes.

Figure 5 General relationship between acid−base pair interaction parameter and factor f, related to the thickness of adsorbed polymer. (●) SVP stabilizing polymer; (■) PCZ stabilizing polymer.

REFERENCES

1. G. D. Parfitt, *Dispersion of Powders in Liquids,* Elsevier Publishing Co., New York, 1969, Chap. 3.
2. A. Doroszowski and R. Lambourne, *J. Colloid Interface Sci.,* **26,** 214 (1968).
3. F. M. Fowkes, *J. Adhesion Sci. Technol.,* **1,** 7 (1987).
4. A. C. Tiburcio and J. A. Manson, *J. Appl. Polym. Sci.,* **42,** 427 (1991).
5. F. M. Fowkes, *J. Adhesion Sci. Technol.,* **4,** 669 (1990).

6. D. R. Lloyd, T. C. Ward, and H. P. Schreiber, *Inverse Gas Chromatography,* ACS Symposium Series 391, American Chemical Society, Washington, DC, 1989.

7. V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions,* Plenum Press, New York, 1978.

8. C. Saint-Flour and E. Papirer, *J. Colloid Interface Sci.,* **91,** 69 (1983).

9. J. Schultz and L. Lavielle, in D. R. Lloyd, T. C. Ward, and H. P. Schreiber, *Inverse Gas Chromatography,* ACS Symposium Series 391, American Chemical Society, Washington, DC, 1989, Chap. 14.

10. J. Lara and H. P. Schreiber, *J. Coatings Technol.,* **63,** 81 (1991).

11. J. Lara and H. P. Schreiber, *J. Appl. Polym. Sci.,* **34,** 1733 (1996).

12. G. DiPaola-Baranyi, C. K. Hsiao, M. Spes, P. G. Odell, and R. A. Burt, *J. Appl. Polym. Sci., Appl. Polym. Symp.,* **51,** 195 (1992).

13. R. O. Loutfy and B. S. Ong, *Can. J. Chem.,* **62,** 2546 (1984).

14. J. M. Braun and J. E. Guillet, *Adv. Polym. Sci.,* **21,** 108 (1976).

15. U. Panzer and H. P. Schreiber, *Macromolecules,* **25,** 3633 (1992).

16. F. L. Riddle and F. M. Fowkes, *J. Am. Chem. Soc.,* **112,** 3259 (1990).

17. D. D. Deshpande, D. Patterson, and H. P. Schreiber, *Macromolecules,* **7,** 630 (1974).

18. C. S. Su, D. Patterson, and H. P. Schreiber, *J. Appl. Polym. Sci.,* **20,** 1025 (1976).

19. M. L. McGlashan and D. J. B. Potter, *Proc. R. Soc. Lond., Ser. A.,* **295,** 271 (1966).

20. J. H. Chen and E. Ruckenstein, *J. Colloid Interface Sci.,* **135,** 496 (1990).

21. F. Bosse, A. Eisenberg, M. El Kindi, Z. Deng, and H. P. Schreiber, *J. Adhesion Sci. Technol.,* **6,** 455 (1992).

22. F. Bosse, A. Eisenberg, Z. Deng, and H. P. Schreiber, *J. Adhesion Sci. Technol.,* **7,** 1139 (1993).

23. J. Kloubek and H. P. Schreiber, *J. Adhesion,* **42,** 87 (1993).

24. N. Casson, in *Rheology of Disperse Systems,* C. C. Mill, Ed., Pergamon Press, Oxford, 1959.

25. S. H. Maron and P. E. Pierce, *J. Colloid Sci.,* **11,** 80 (1956).