Infrared Spectroscopic Analysis of Complex Polymer Systems

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Synopsis

A procedure has been developed for the analysis of complex polymer systems, using infrared spectroscopy. Its application to the analysis of styrene–butadiene–styrene triblock copolymers hydroxylated in the solid phase by reaction with peracetic acid is described. Twenty-two frequencies of analytical interest were found sufficient to describe the infrared spectrum of the reacted polymer and were used to estimate the concentrations of the 12 components (functional groups) found to be present. A least-squares solution of the Lambert-Beer law equations was used to determine the 12 concentrations of interest. The errors associated with the regression and with the uncertainties in the determination of the absorptivities were determined using model compounds with the functional groups in approximately similar environments to those found in the polymer. With this procedure, the concentrations of the major components could be determined to within ±30%, which was sufficient to determine the effects of diffusion on the solid-phase reaction process.

INTRODUCTION

The use of infrared spectroscopy for qualitative and quantitative analysis of polymers is well established.[1] However, in only a few cases has it been applied to the analysis of complex polymer systems such as polybutadienes[2,3] and polybutadiene–polystyrene copolymers,[4] where there are only three or four components involved. It is the purpose of this paper to describe the development of an infrared spectroscopic procedure for the analysis of a polymer which contains at least 12 components.

In this case, the analysis scheme was considered to be a model fitting procedure rather than a strict analytical method. The complex spectrum of the polymer was considered to be composed of the spectra of certain pure "calibration" compounds superimposed upon each other. The correlation coefficients which gave the best fit to the spectrum of the polymer were considered to be the relative amounts present in the polymer sample of each of the functional groups represented by the calibration compounds. Although many of the details of the precedure are relevant only to the particular polymer investigated (hydroxylated styrene–butadiene–styrene block copolymer), the approach taken is of more general interest.

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EXPERIMENTAL

Styrene–butadiene–styrene triblock copolymers were hydroxylated by utilizing the reaction of the polybutadiene phase with preformed peracetic acid to form an epoxide product which was then cleaved (by water or acetic acid) to the desired 1,2-glycol structure:
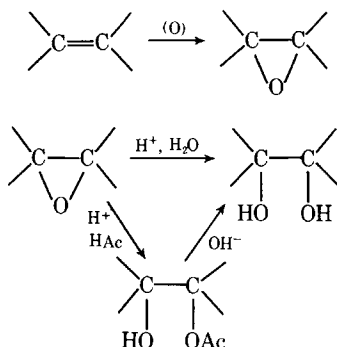
Since the hydroxylation of the copolymer was carried out with the polymer in the bulk state (as a film), the formation of intermolecular ethers (crosslinks) occurred in addition to the more common side reactions: epoxide rearrangement to carbonyls and to substituted tetrahydrofuran rings (intramolecular ethers). Since the rearrangement to ethers (either intra- or intermolecular) may occur simultaneously with dehydration, a number of different substituents are possible in the rearranged product, and, for example, both saturated acyclic ethers and vinyl acyclic ethers are equally possible.

EQUATIONS

The basis for the analysis was the Lambert-Beer law extended to a multicomponent system which at a single frequency ν is:

$$\log_{10} T_0/T = A^\nu = a_1^\nu b c_1 + a_2^\nu b c_2 + \ldots\ldots + a_m^\nu b c_m = b \sum_{i=1}^{m} a_i^\nu c_i \qquad (1)$$

where A = absorbance, T = transmittance at the peak maximum, a_i = absorptivity of component i, T_0 = transmittance at the baseline, C_i = concentration of component i (moles/cm^3), b = path length (cm), and m = the number of components. This equation is normally written at m frequencies characteristic of the components in the sample, and the resulting set of m equations in m unknowns is solved (if the absorptivities and path length are known) to determine the values of the m concentrations. The frequencies chosen for the analysis are those at which just one of the components absorbs strongly with only minor interfering absorptions of the other components, i.e., that set of frequencies which maximizes the absolute value of the determinant of the matrix of absorptivity coefficients of the m linear equations. This approach was used in the above-cited analyses[2-4] with reasonable precision.

In order to improve the precision of the multicomponent analytical scheme, an overdetermined system of equations was used with a least-squares solution determined by standard techniques.[5] Herschberg and Sixma[6] and

Bauman[7] have discussed the applicability of overdetermined systems in absorption spectroscopy.

Using matrix notation and defining $X_i = bC_i$, the set of n linear equations in m unknowns corresponding to the Lambert-Beer law written at n frequencies for m components ($n > m$) is

$$\mathbf{A} = \mathbf{aX} \tag{2}$$

where $\mathbf{A}$ = vector of absorbances of length n, $\mathbf{a}$ = matrix of absorptivities ($n \times m$) and $\mathbf{X}$ = vector of area concentrations [moles/cm^2] of length m.

The least-squares solution to eq. (2) is obtained by minimizing the sum of squared residuals. The resulting average values for the X_i, $\langle \mathbf{X} \rangle$ in vector notation, are defined by

$$\langle \mathbf{X} \rangle = (a^T a)^{-1} \, \mathbf{a}^T \mathbf{A} \tag{3}$$

where T denotes transpose and -1 denotes inverse. The residuals $\mathbf{r}$ are defined by

$$\mathbf{r} = \mathbf{A} - \mathbf{a} \, \langle \mathbf{X} \rangle. \tag{4}$$

That this is a plausible approach can be illustrated by application of a theorem of Jacobi[6]: the least-squares solution $\langle X \rangle$ equals the one obtained by taking a weighted mean of the solutions of all combinations of m equations that can be selected from the n rows of (A, a), weights being allotted proportionally to the square of the determinant of the coefficients of each combination, that is, proportionally to the reliability of each solution by the criterion mentioned before.

Herschberg and Sixma[6] have pointed out that the validity of the least-squares solution, eq. (3), assumes an independently known a. However, they also demonstrated that the more formally correct solution (since coefficients of a are subject to the same measurement errors) is not significantly different from this least-squares solution.

The X_i values were converted in this work into true "concentrations" (independent of spectrum sample size) using polystyrene (phenyl group) as an internal standard:

$$F_i = \frac{\langle X_i \rangle N}{X_{\text{phenyl}}} \tag{5}$$

where F_i is the number of moles of component i per 100 moles of unsaturation present in the original sample before reaction, and N is the ratio of moles of phenyl groups to 100 moles of unsaturation in the copolymer (here, $N = 19.89$).

The standard error of the estimate σ is easily calculated to be

$$\sigma = \sqrt{\frac{\sum_{j=1}^{n} r_j{}^2}{n - m}} = \sqrt{\frac{\mathbf{r}^T \mathbf{r}}{n - m}}. \tag{6}$$

The standard error of estimate is then utilized to calculate E_i', the standard deviation of each value of the area concentration $\langle X_i \rangle$, due solely to the regression

$$E' = \sigma \sqrt{(\mathbf{a}^T\mathbf{a})^{-1}} \qquad\qquad (7)$$

in matrix notation.[5] The error calculations are discussed more fully in the appendix.

All calculations were performed with the aid of an IBM 1130 computer.

SPECTRA RECORDING

All spectra were recorded using a Perkin-Elmer Model 521 grating infrared spectrophotometer. The spectra were run at room temperature with the instrument in the normal operating mode, with a reproducibility of ±0.5% transmittance with a suitable degree of resolution.

For those films thinner than about 25 microns, the complete spectrum was obtained without further preparation. For thicker films, however, samples of the films were ground at liquid nitrogen temperatures to a fine powder and dispersed in carbon disulfide. The spectra were then recorded of the carbon disulfide suspensions in a 0.5-mm sealed liquid cell. The use of an internal standard obviated the need for knowing the thickness of the film or the concentration of dispersed polymer.

QUALITATIVE ANALYSIS

Fundamental to the use of the analytical scheme developed here is the assumption that all of the components present in the sample are considered in the infrared model of the system. This necessitates careful qualitative analysis of the spectrum combined with a knowledge of the chemistry of preparation of the sample. The use of other analytical techniques is also essential, although in this work the crosslinked nature of the film and the particular functional groups present rendered the other available procedures (e.g., carbon-13 NMR) of little value.

The spectrum of bulk hydroxylated styrene–butadiene–styrene block copolymer is shown in Figure 1, and the assignments are described in Table I.

The uncertainties noted above with regard to the nature of the substituents on the ether groups (cyclic and/or acyclic ethers) present in the reacted polymer resulted in the appearance of a broad peak in the infrared spectrum, made up of smaller absorptions due to each individual structure, in the region characteristic of that structural type. This was particularly true of the substituted tetrahydrofuran peak near 1067 cm^{-1}.

From the qualitative analysis of the reacted copolymer, the presence of 12 distinct components was detected, and 22 absorptions of analytical value were found. For the spectra obtained on samples in the absence of CS_2, all 22 absorptions could be used. However, the remaining spectra were obtained of CS_2 suspensions so that four of these 22 absorptions (1657, 1637, 1602, and 1493 cm^{-1}) were completely masked by solvent absorptions. Therefore, the system of equations used for analysis was either 22 or 18 equations in 12 unknowns, depending on the sample.
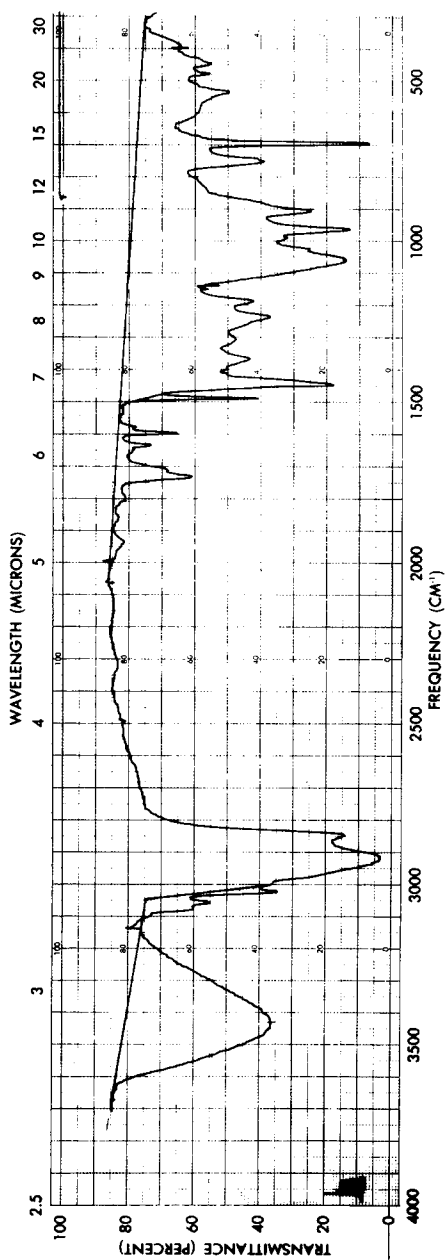
Fig. 1. Infrared spectrum of typical surface hydroxylated styrene–butadiene–styrene block copolymer TR-41-2443. Reaction conditions: 40°C, 60 min, 71.1% acetic acid.

TABLE I
Peak Assignments; Spectrum of Surface Hydroxylated
Styrene-Butadiene-Styrene Block Copolymer [Figure 1]

Frequency ν, cm^{-1}	Major functional group	Nature of absorption	Model compound	Reference	Notes
3430	hydroxyl	O—H stretch	poly(vinyl alcohol)	8	
3061	phenyl	C—H stretch	polystyrene	9	
3029	phenyl	C—H stretch	polystyrene	9	
3004^f	cis alkene	C—H stretch	cis-1,4-poly- butadiene	4	
2950– 2850^f	methylene, methine	C—H stretch	—	10	
1737	acetate	C=O stretch	poly(vinyl acetate)	11	
1710	ketone carbonyl	C=O stretch	—	10	
1657	cis alkene	C=C stretch	cis-1,4-poly- butadiene	4	
1637	vinyl alkene	C=C stretch	1,2-poly- butadiene	4	
1602	phenyl	ring vibration	polystyrene	9	
1493	phenyl	ring vibration	polystyrene	9	
1455^f	methylene, methine	C—H bending	—	10	
1378^f	acetate	CH$_3$ deformation	poly(vinyl acetate)	11	e
1308	cis alkene	C—H bending	cis-1,4-poly- butadiene	4	
1240	acetate	ester skeleton	poly(vinyl acetate)	11	
1240	phenyl ether	C—O stretch	diphenyl ether	12, 13	a, b
1210	vinyl ether	C—O stretch	1-methoxycyclo- hexene	12, 13 15	a, b
1090	saturated acyclic ether	C—O stretch	dicyclohexyl ether	12, 13 15	c
1067	tetrahydro- furan ring	ring stretch	see note d	see note d	d
1025	phenyl	C—H bending	polystyrene	9	
995	vinyl alkene	C—H out-of- plane defor- mation	1,2-poly- butadiene	4	
967	trans alkene	C—H out-of- plane defor- mation	trans-1,4-poly- butadiene	4	
910	vinyl alkene	CH$_2$ out-of- plane defor- mation	1,2-poly- butadiene	4	e
882	epoxy	asymmetric ring stretch	2,3-epoxy- butane	12, 14	
807	epoxy	ring deforma- tion	2,3-epoxy- butane	12, 14	
757	phenyl	C—H out-of- plane defor- mation	polystyrene	9	

(continued)

TABLE I (*continued*)

Frequency ν, cm^{-1}	Major functional group	Nature of absorption	Model compound	Reference	Notes
737	cis alkene	C——H out-of-plane deformation	cis, 1,4-polybutadiene	4	
699	phenyl	C——H out-of-plane deformation	polystyrene	9	

a Both the phenyl ether and vinyl ether absorptions refer to the half ether [$\geqq$C——O] structures.

b The maximum of these peaks appeared sometimes near 1260 cm^{-1} and 1195 cm^{-1} due to interfering absorptions from hydroxyl and tetrahydrofuran groups. When these interfering absorptions were subtracted out, the maximum residual absorbance appeared at 1240 cm^{-1} and 1210 cm^{-1}, respectively.

c The interfering C——O absorption of hydroxyl groups was relatively small.

d A number of model compounds were used to make this assignment: tetrahydrofuran, 1,5-bis(tetrahydro-2-furyl)-3-pentanol,[12] linalool oxide [2-vinyl-2-methyl-5-(1'-hydroxy-1'-methylethyl)tetrahydrofuran],[16] and other terpenoid derivatives.[17] This assignment was complicated by the multiplicity of tetrahydrofuran structures present.

e The interfering absorptions of the asymmetric ring vibration at 908 cm^{-1} and the 1364 cm^{-1} CH$_2$ wagging vibration of tetrahydrofuran were relatively small.

f Not used in analytical scheme.

CALIBRATION

Compounds

The main reason that this analysis had to be considered as a model-fitting procedure was the absence of perfectly suitable calibration compounds for the determination of the absorptivities (**a**). Instead of polymeric compounds containing the functional group of interest in an environment comparable to that found in the surface hydroxylated sample, low molecular weight compounds had to be used on occasion, containing the functional group in a slightly different intramolecular environment. Even where polymeric calibration compounds were available, because of the properties of the polymer, spectra for some of them had to be run in solution (solvents CS$_2$ and CHBr$_3$) rather than as films. Therefore, there were differences in the intermolecular environments (state) between sample and calibration compounds. The calibration compounds are listed in Table II.

An additional reason that this scheme must be considered a model-fitting procedure is that the broadness of the ether peaks made it difficult to compute the background interferences due to other absorptions at neighboring frequencies. The net result would be a high estimate of the absorbance at these neighboring peaks, attributed in error to the component(s) that absorb strongly at that frequency. There would also be uncertainity in the true value of the number of other groups giving rise to the broadened peak.

The assumption of Szymanski[13] in dividing the absorption of each asymmetric ether into two components, one from each half of the ether linkage, was extended here to the quantitative analysis scheme. Each half of the ether linkage was assumed to give rise to a separate absorption peak with its own extinction coefficient (absorptivity). The spectra were then analyzed on the basis of moles of carbon–oxygen bonds, independent of the nature of the

TABLE II

Calibration of IR Quantitive Analysis

| Functional group	Sample molecular environment[a]	Calibration compound	Calibration molec. environ.	State[b]
Phenyl	—CH₂—CH—CH₂— (with phenyl ring)	polystyrene	identical	solution[d]
Cis alkene	HC=CH / —H₂C, CH₂—	cis-1,4-poly-butadiene	identical	solution[d]
Trans alkene	—H₂C, CH=CH, CH₂—	trans-1,4-poly-butadiene	identical	solution[d]
Vinyl alkene	—CH₂—CH— / CH ‖ CH₂	1,2-polybutadiene	identical	solution[d]
Hydroxyl	—CH₂—CH—CH—CH₂— OH OH	poly(vinyl alcohol)/copoly-(vinyl acetate)	—CH₂—CH—CH₂—CH— OH OH	film
Acetate	—CH₂—CH—CH—CH₂— OH OAc	poly(vinyl acetate)	—CH₂—CH— OAc	film
Carbonyl	—CH₂—CH—CH₂— O	literature value used (methyl-n-hexyl ketone)		
Epoxy	—CH₂—CH—CH—CH₂— O	2,3-epoxy butane	CH₃—CH—CH—CH₃ O	solution
Five-membered cyclic ether	(tetrahydrofuran ring)	tetrahydrofuran	(ring)	solution
Saturated acyclic ether	—H₂C, HC—O—CH, —H₂C	dicyclohexyl ether	S—O—S (cyclohexyl)	solution
Vinyl ether	—HC, C—O—CH, —H₂C	1-methoxy-cyclo-hexene	(ring)—O—CH₃	solution
Phenyl ether	HC—O—(phenyl)	diphenyl ether	(phenyl)—O—(phenyl)	solution

a This is the assumed molecular environment.

b Solvents: carbon disulfide, 3800–2900 cm⁻¹, 2000–1700 cm⁻¹, 1350–625 cm⁻¹, bromoform, 1700–1350 cm⁻¹.
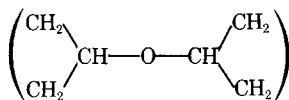
c See the body for description of the ether structures.

d Some of the absorptivities were determined in solid film by comparison with known absorptivities.

substituents on the second carbon of the ether linkage. For example, asymmetric vinyl ethers were assumed to be made up of two parts; the saturated part

$$\left(—O—CH\begin{smallmatrix} CH_2 \\ \\ CH_2 \end{smallmatrix} \right)$$
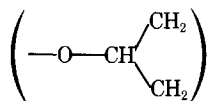
with absorbance maximum at 1210 cm⁻¹. On the other hand, symmetric ethers gave rise to a single peak the absorptivity of which was halved to get the absorptivity per mole of C—O bonds. For example, acyclic saturated ethers

$$\left(\begin{smallmatrix} CH_2 \\ \\ CH_2 \end{smallmatrix}CH—O—CH\begin{smallmatrix} CH_2 \\ \\ CH_2 \end{smallmatrix} \right)$$

have a single absorbance maximum at 1090 cm^{-1}. The absorptivity of the saturated part of the vinyl ether was assumed to be the same as the halved absorptivity of this symmetric acyclic saturated ether. Hence, only three acyclic ether structures
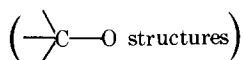
$$\left(\!\!\!\overset{\diagdown}{\underset{\diagup}{C}}\!\!-\!\!O \ \ \text{structures} \right)$$

and only three sets of absorptivities were needed to characterize fully the six possible acyclic ether structures.

Except for the O—H stretching peak at 3430 cm^{-1}, the height of the peak was used to define the absorbance at that frequency. For the O—H stretching peak, however, the area under the peak was used. On the assumption[10] that the absorbance at each wave number in this peak reflects a certain number of hydroxyl groups with a certain hydrogen bond strength, the maximum absorbance merely reflects that hydrogen bond which is most numerous. Therefore, shifts in the maximum peak indicate only changes in the distribution of hydrogen bonding. Hence, the area under the peak should reflect the number of hydroxyls present irrespective of the type of hydrogen bonds present or the location of the peak. Thus, the area of the OH peak in the hydroxylated SBS samples could be compared to the area of the OH peak in poly(vinyl alcohol)–poly(vinyl acetate) copolymer films which was centered at 3340 cm^{-1}, a 90 cm^{-1} shift.

Because only a small amount of carbonyl (less than 1%) was present in our spectra, a literature value of the absorptivity at 1710 cm^{-1} was used.[18] The errors, so involved, were assumed to be of little consequence.

Procedure

For the calibration compounds in solution, spectra were recorded for five concentrations. The least-squares linear correlation coefficient (and 95% confidence interval) of absorbance on concentration was determined at each frequency of interest using an IBM 1130 computer. If the F-value statistic was not high enough, the correlation coefficient was considered to be not significantly different from zero (95% confidence). The absorptivity was then calculated directly from the correlation coefficient.

For the compounds used as films, spectra were recorded for a number of films of varying thickness. The weights of 1.345-cm^2 samples were determined using a Sartorius microbalance, and the least-squares linear correlation coefficient of absorbance on weight was determined using the computer, from which the absorptivity was then also calculated.

The baselines were drawn in all spectra to eliminate any interfering absorptions that could not be accounted for in the final analytical scheme. The baseline used was that logical baseline which gave the best fitting correlation of absorbance on concentration or film weight.

Since each polybutadiene used for calibration contained some of the other types of double bonds, the procedure of Silas et al.[3] and their assumption of 100% unsaturation was used to get the true absorptivities for each of the three double-bond types. A similar procedure was used in determining the hydroxyl absorptivities from the poly(vinyl alcohol)–poly(vinyl acetate) co-

TABLE III
Typical Results and Errors

Component	Per cent of original unsaturation (F_i)	Error due to regression (E_i')	Error due to propagation from a (E_i'')	Total error (Ex_i)
Phenyl	19.89 (assumed)	±1.52	±6.95	±7.11
Cis alkene	15.81	±8.99	±4.26	±9.95
Trans alkene	33.36	±2.79	11.52	±11.86
Vinyl alkene	12.20	±2.26	6.52	±6.90
Hydroxyl	11.77	± .64	2.90	±2.97
Epoxy	8.79	±4.22	2.49	±4.90
Tetrahydrofuran	4.49	±1.51	1.12	±1.88
Saturated ether	3.78	±2.07	1.35	±2.47
Vinyl ether	1.28	±0.69	0.36	±0.78
Phenyl ether	1.31	±0.90	0.54	±1.05
Carbonyl	0.31	±2.15	1.46	±2.60
Acetate	0.15	±1.45	1.50	±2.09

polymer films (the copolymer was used to avoid interferences from the crystalline environment present in a film of poly(vinyl alcohol) homopolymer) by assuming that the absorption of hydroxyl at 1737 cm^{-1} was zero in the copolymer films.

TYPICAL RESULTS AND ERRORS

Typical results are shown in Table III for a 90-micron-thick film reacted at 40°C for 80 min in a reaction bath of 71.1% acetic acid, 22.8% water, 5.1% peracetic acid, and 1% sulfuric acid. The spectrum was obtained on a dispersed sample.

The errors are generally in the range of 30–40%, with somewhat larger errors in the "concentrations" (F_i values) of the components present in only minute amounts. These errors are quite reasonable considering the complexity of the spectrum analyzed, and are sufficiently small to enable conclusions to be drawn with regard to the effect of diffusion limitations on the composition of the films after reaction.[19]

The relatively larger error in the "concentration" of the cis double bonds is consistent with the established difficulty in analyzing for cis by infrared spectroscopy.[4] Although the major factor contributing to the total error was the propagation of errors in the absorptivities to the final answer, improvements in the calibration procedure were not warranted. The unknowns in the use of low molecular weight compounds as models for the absorption of functional groups in the polymer are such that any reduction in the determinate error would be outweighed by these indeterminate errors.

CONCLUSIONS

Although many of the details of this analytical scheme are relevant only to the particular system investigated, the successful adaptation of infrared spec-

troscopy to complex polymer systems is of widespread value.   Among the improvements demonstrated here are: (a) the use of the analytical scheme as a model-fitting procedure relating the spectra of model "calibration" compounds to the spectrum of the complex sample; (2) the use of an overdetermined system to improve precision; (3) the use of an internal standard to eliminate the necessity of measuring film thickness.   Further benefit arises by having error analysis an integral part of the computation scheme.

APPENDIX

Error Calculations

Two sets of errors were distinguished in the calculation procedure.   One set was due to the least-squares solution of an overdetermined system, eq. (7), and one set due to the propagation of uncertainties in the value of each individual absorptivity.   This latter set of errors was calculated using standard formulas for propagation of errors.   The geometric mean of the two sets of errors was considered to be the best estimate of the errors in the set of concentrations $\langle \mathbf{X} \rangle$.

The errors propagated from the absorptivity matrix were calculated according to

$$\mathbf{E}'' = (a^T a)^{-1} \sqrt{\mathbf{A}^T \mathbf{E} \mathbf{E}^T \mathbf{A} + \langle \mathbf{X} \rangle^T \mathbf{E}'''^T \mathbf{E}''' \langle \mathbf{X} \rangle} \tag{8}$$

where $\mathbf{E}''$ = errors in $\langle \mathbf{X} \rangle$ propagated from the set of errors $\mathbf{E}$ in $\mathbf{a}$, $\mathbf{E}$ = matrix of errors in a, and $\mathbf{E}'''$ = errors in $[\mathbf{a}^T \mathbf{a}]$ propagated from $\mathbf{E}$, calculated according to eq. (9); dimension $(m \times m)$.

Each element of $\mathbf{E}'''$ was calculated according to

$$\mathbf{E}_{l,K}''' = \sqrt{\sum_{j=1}^{n} [(E_{j,l} a_{j,k})^2 + (E_{j,k} a_{j,l})^2]} \tag{9}$$

where $a_{j,k}$ = the element of the absorptivity matrix $\mathbf{a}$ corresponding to frequency $\nu = j$ and component k, and $E_{j,k}$ = the corresponding element of the error matrix $\mathbf{E}$.

The combined errors in $\langle X \rangle$, $\mathbf{E}_x$, were then given by

$$\mathbf{E}_x = \sqrt{\mathbf{E}''^T \mathbf{E}'' + \mathbf{E}'^T \mathbf{E}'} \tag{10}$$

where $\mathbf{E}'$ is the set of errors due solely to the regression.

The elements of $\mathbf{E}$ were computed directly from the correlations of absorbance on concentration or film weight.

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