Near-IR Fiber-Optic Probe for Electrolytes in Aqueous Solution

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Fiber-optic probes for electrolytes have been developed based on the perturbations of near-IR water bands. These probes are readily fabricated by leaving a small gap between two fibers for the solution to enter. Single and multiple electrolytes and temperature can be determined can be determined from their perturbations of the water bands. The concentrations are calculated by linear and multilinear regression of absorbances at selected wavenumbers and by principal component regression using entire spectra. The standard errors of concentrations are different for different electrolytes and are dependent on the range of the concentrations. The larger the perturbations caused by the electrolyte, the smaller the standard errors. Standard errors less than 10 mM are obtainable for concentrations in the range 0–1 M. These fiber-optic probes have potential uses in remote sensing of electrolytes, in process control, and in hostile electrical environments.

INTRODUCTION

There have been numerous attempts to develop fiber-optic sensors for continuous monitoring and remote sensing of electrolytes due to their importance in process control and in the environment. Among these are fluorescence fiber-optic sensors based on the effect of electrolytes (cations or anions) on the fluorescence of reagents immobilized on the distal end of fibers. Several fiber-optic sensors have been developed for the measurements of halide ions based on the fluorescence quenching.[1-3] There are also fluorescence fiber-optic sensors available for the determinations of cations such as selective sensors for single ions[4-9] or sensors for multiple cations.[10-13] Several ions can be measured simultaneously with multifiber sensors (so called optrode arrays)[14,15] or by time-resolved fluorescence with single sensor.[11] Many of these sensors have some drawbacks including difficulty in fabrication, limited life times, and the need for maintenance and special measurement conditions (such as pH and temperature). While selective fiber-optic sensors are needed for many applications, simple and universal sensors are often useful for monitoring electrolytes in aqueous solutions.

Compared to its fluorescent counterparts, absorbance sensors have received much less attention.[16] Perturbations of the near-IR spectrum of water by electrolytes are well-known and have been used in both qualitative and quantitative analyses. Some electrolytes, such as NaCl and NaOH, in aqueous solutions have been determined using near-IR spectra.[17-20] However, all of these measurements were made using a cuvette for a single electrolyte, and they were not applied to remote monitoring.

In the present study, we developed fiber-optic probes based on the perturbations of near-IR water bands by electrolytes. Several electrolytes were determined using these probes. We also extended this technique from single electrolyte measurements to multicomponent analyses in which simultaneous measurements of several electrolytes were performed. Both electrolyte and temperature were also determined simultaneously. These fiber-optic probes are simple and readily fabricated. In addition, they are universal and can be used in remote sensing of electrolytes in aqueous solutions, especially in the strong electrical environments.

EXPERIMENTAL SECTION

Fabrication of Fiber-Optic Probes. Anhydroguide-PCS optical fiber from Fiberguide Industries (Stirling, NJ) was used in this investigation. Diameters for the silica core, polymer cladding, and nylon jacket were 400, 500, and 600 μm, respectively. Fiber-optic probes were readily fabricated by leaving an open space between two fibers for the solution. Three types of fiber-optic probes were fabricated and tested. In the open type of probe, two fibers were arranged in a coaxial and face-to-face position with a small gap between the fiber ends. In the reflection type of probe, a first surface reflecting mirror was used to reflect the light from the source fiber to the detection fiber. The diagrams of the above two types of probes can be seen elsewhere.[21] These two types of probes can be dipped into solution for the measurements. Figure 1 shows the cell type probe, in which a small amount of solution (about 0.3 mL) can be placed in the cell between two fibers held across an indentation in a plexiglass plate. The path length is about 1 mm for all the probes.

Electrolyte Solutions. All the solutions were prepared using distilled water and analytical-grade reagents. Standard solutions were prepared in two ways. For one method, a complete set of standard solutions was prepared from the starting materials. For the other method, we began with one standard solution and changed its concentration by titration.

Measurement Configuration. The optical attachment for interfacing the fiber-optic probes to the near-IR spectrometer was built in-house.[21] Light from the spectrometer was reflected by a first surface reflecting mirror and focused with a silica lens onto the source fiber. The detection fiber was placed directly in

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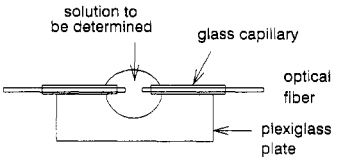

Figure 1. A diagram of fiber-optic probe of cell type.

front of the optical window of the detector and light was directed to the target without using a focusing lens.

The open and reflection types of probes were immersed into the solution in a beaker. The temperature of the solution in the beaker was controlled by pumping water from a thermal circulator through a jacket surrounding the beaker. The precision of the temperature control was ±0.05 °C or better.[21] The solution in the tempering beaker was stirred during the time of measurement. For the cell type of probe, all the measurements were made at room temperature (23.0 ± 0.5 °C). A fresh sample was pipetted (into the cell) for the measurement of each spectrum.

Spectral Measurement. Spectra were measured on a BIO-RAD FTS-40N near-IR spectrometer with an InSb (Indium Antimonide) detector (BIO-RAD, Digilab Division, Cambridge, MA). Single beam spectra of fibers were measured with the probes in air and were used as background. Spectra were measured from 5350 to 9000 cm^{-1} with 64 scans at a resolution of 16 cm^{-1}. The digitized data were acquired with a BIO-RAD SPC 3200 data station and imported to a personal computer for further processing.

Data Processing. In order to account for small changes in (room) temperature, three spectra were measured for each sample. Two of the three spectra were randomly selected and used in the standard (training) set; the other spectrum was used in the unknown (validation) set. The standard set was used to develop the models to predict the unknown set.

The algorithm used for principal component regression (PCR) employed the successive average orthogonalization developed by Donahue and Brown.[22] The standard errors of estimation and prediction (SEE and SEP) for the individual components are calculated as follows:

$$\mathrm{SEE}_i = \left[\frac{\sum (C_i - \hat{C}_i)^2}{m - t}\right]^{1/2}$$

$$\mathrm{SEP}_i = \left[\frac{\sum (C_i - \tilde{C}_i)^2}{m}\right]^{1/2}$$

where C_i, $\hat{C}_i$, and $\tilde{C}_i$ are the actual, estimated, and predicted concentrations for the ith component, m is the number of mixtures, and t is the number of eigenvectors used in the PCR. The number of eigenvectors that are used is determined by a frac_i indicator, which is the fraction of the variance fitted by ith eigenvector compared to the total fitted by it and the remaining eigenvectors.[23] The eigenvector producing the lowest frac_i indicates that this one and all the remaining ones represent noise and that they should not be used in the model.

The multilinear regression (MLR) was performed using a stepwise algorithm developed by Honigs et al.,[24] in which the absorbances at all wavenumbers (477 points) were used and four passes were performed for the selection of an optimum set of analytical wavenumbers.

In a single electrolyte solution, in which the changes in the absorbances were linear with concentration, linear regression (LR) using absorbances at selected wavenumbers was performed to calculate the concentrations. In two-component systems (NaCl and temperature, NaCl and HCl), there are wavenumbers at which the perturbations of one component (temperature and HCl) are zero, i.e. isosbestic points. The absorbances at the wavenumbers for the isosbestic points were used to calculate the concentrations of the second component by linear regression (LR_{iso}). In LR and LR_{iso} the spectra were baseline zeroed at 9000 cm^{-1} to remove possible baseline shifts, while in PCR and MLR original spectra were used and the baseline shift was accounted for by the models.

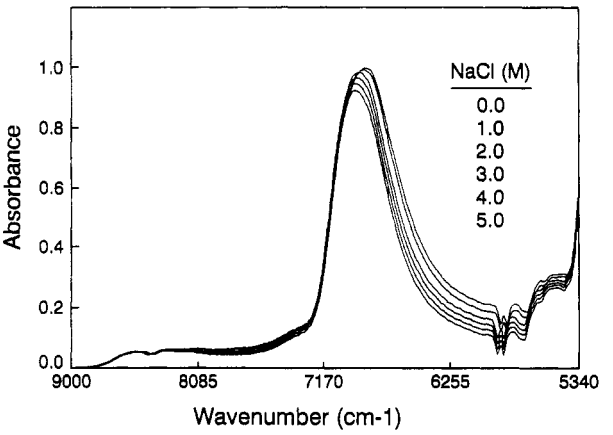

Figure 2. Near-IR spectra of NaCl solutions at different concentrations, measured with a cell type of probe.

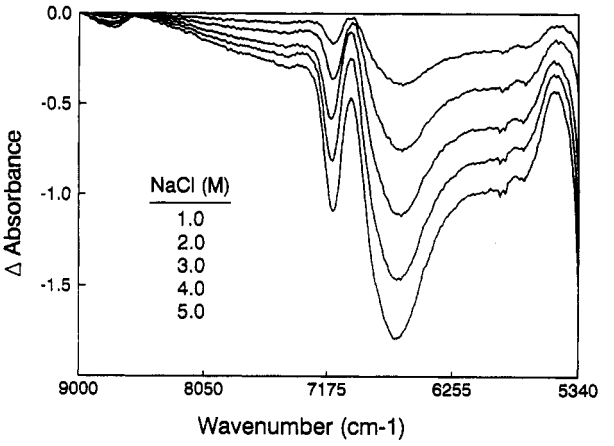

Figure 3. Near-IR difference spectra of NaCl solutions at different concentrations, measured with cell type of probe. The spectrum of water is used as reference and is subtracted from the spectra of NaCl solutions.

RESULTS AND DISCUSSION

Measurement of NaCl. Figure 2 shows the near-IR spectra of NaCl solutions at different concentrations; the spectra are baseline zeroed at 9000 cm^{-1}. The perturbations of the water band by NaCl are very clear. When the concentration of NaCl increases, the intensity (in absorbance) of the water band decreases, the band becomes narrower and shifts to higher wavenumber. These changes are caused by the decrease in water concentration in NaCl solutions and the hydrations of ions.

We can also examine the perturbations of NaCl on the water band using the difference spectra. Figure 3 shows the difference spectra of NaCl solutions at different concentrations; the spectrum of water is used as reference and is subtracted from the spectra of NaCl solutions. It is very clear that the perturbations by NaCl are negative over the entire spectral region. In contrast to NaCl, some electrolytes decrease the intensity of the water band in some wavenumber regions but increase the intensity in other regions. Among these electrolytes are HCl, $NaHCO_3$, and Na_2CO_3; their effects on the water band will be discussed later in this article.

As can be seen in Figure 3, the changes in the absorbance are reasonably linear with the concentration of NaCl. Therefore, linear regression using absorbances at selected wavenumbers can be performed to calculate the concentration of

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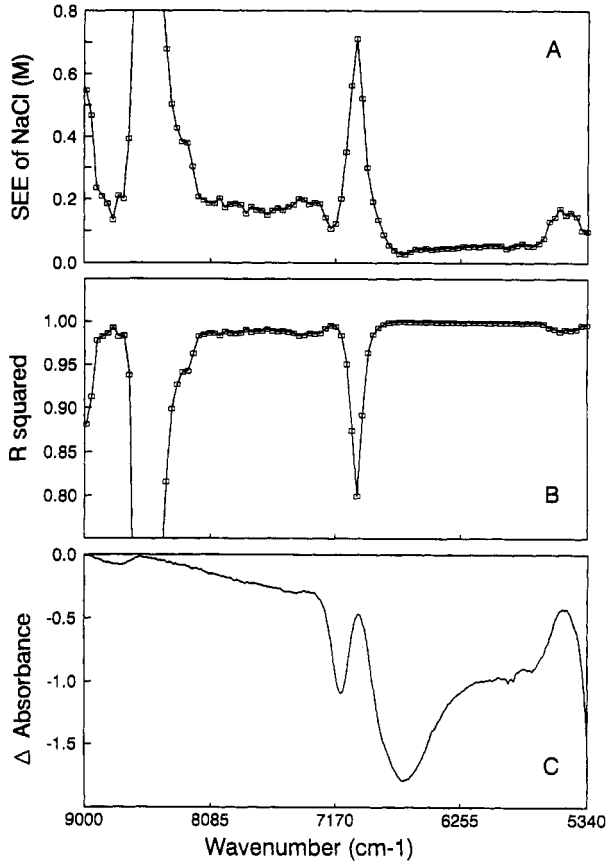

Figure 4. Results of linear regression between NaCl concentration and absorbance, as compared to a difference spectrum: (A) standard error of estimation of NaCl concentration; (B) the square of the correlation coefficient; (C) difference spectrum of 5 M NaCl minus water. Measurements were made with a cell type of probe.

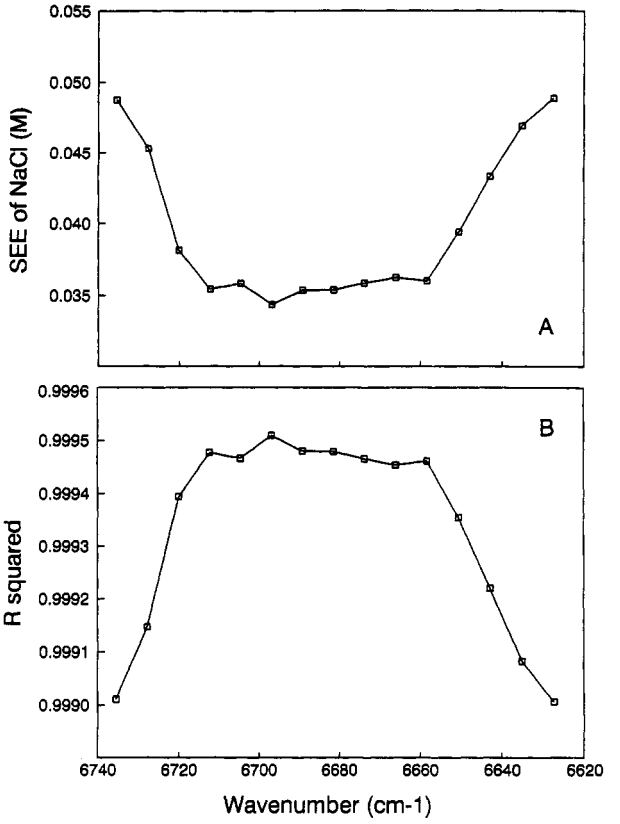

Figure 5. Best wavenumber region for linear regression between NaCl concentration and absorbance: (A) standard error of estimation of NaCl concentration; (B) the square of the correlation coefficient. Measurements were made with a cell type of probe.

NaCl. The results of linear regression over the entire spectral region are compared with a difference spectrum in Figure 4. It can be seen that small SEE's are obtained over the regions which have large perturbations. Overall, the region between 6550 and 6750 cm^{-1} which is shown in Figure 5 gives the smallest SEE's and largest R^2. As can be seen, very good linear correlations are obtained in this region.

The above discussion indicates that the concentration of NaCl can be calculated by performing a linear regression using the absorbances at selected wavenumbers. This is true when the concentrations of electrolyte are high and the measurements are made at a constant temperature. In linear regression only one variable is included in the calculation. However, the changes in concentrations of an electrolyte will not only cause perturbations to the water band but also cause changes in the refractive index of solution. When measurements were made using the cell type of probe, fluctuation in room temperature imposes the effect of temperature on the spectra. When the concentrations are low and perturbations by the electrolyte are small, the noise in the absorbance may become significant. Therefore, we expect that the principal component regression (PCR) and multilinear regression (MLR), which make it easy to account for more than one variable, will give better results in the calculation of concentration.

Principal component regression was used to calculate NaCl concentrations with different wavenumber regions of the spectrum and with the entire spectrum from 5350 to 9000 cm^{-1}. The latter always gave the best results, and thus, PCR was performed using the entire spectra. Three eigenvectors are indicated for NaCl concentrations from 0 to 5 M, and four for NaCl from 0 to 1 M and 0 to 0.1 M. The SEP's obtained are 0.013, 0.008, and 0.003 M for these three concentration ranges, respectively.

Multilinear regressions were also performed to select the analytical wavenumbers for the calculation of NaCl concentrations. It is indicated that four, three, and two wavenumbers are needed for NaCl concentrations from 0 to 5 M, 0 to 1 M, and 0 to 0.1 M, respectively. The SEP's obtained are 0.028, 0.025, and 0.004 M, respectively.

More than one eigenvector and wavenumber are used in PCR and MLR, indicating that the change in NaCl concentration causes changes in spectra in more than one way. It is interesting to see that the numbers of eigenvectors and wavenumbers used in PCR and MLR are different for the three concentration ranges.

Results of Single Electrolyte Measurements. The results of all measurements for single electrolyte are listed in Table I. The concentrations were calculated by PCR and MLR. Two points should be noticed from this table. (i) For the same concentration range of NaCl measured with different types of probes (e.g., NaCl 0 to 1 M with all the three types of probes), the standard errors are very close to each other. (ii) For the same concentration range, different standard errors are obtained for different electrolytes. As will be seen later (in Figures 7 and 9), smaller standard errors are obtained for the electrolytes which have larger perturbations, i.e., the sequence of perturbations is HCl > NaCl > $NaHCO_3$ and the sequence of errors is HCl < NaCl < $NaHCO_3$. Provided that the noise level of absorbance measurement remains the same, the larger perturbations, give larger signal-to-noise ratios, thus, smaller standard errors are obtained.

Simultaneous Measurement of NaCl and Temperature. We have demonstrated the feasibility of the fiber-optic probes for the measurement of a single electrolyte. In another study, we used the same probes (open and reflection types) for the measurement of temperature.[21] In this study,

Table I. Results for the Measurements of Single Electrolytes[a]

			PCR			MLR		
electrolyte	concn (M)	probe	no. VT[b]	SEE (M)	SEP (M)	no. WN[c]	SEE (M)	SEP (M)
NaCl	0–5	cell	3	0.016	0.013	4^A	0.027	0.028
NaCl	0–1	cell	4	0.009	0.008	3^B	0.020	0.025
NaCl	0–0.1	cell	4	0.003	0.003	2^C	0.006	0.004
NaCl	0–1	reft	5	0.011	0.011	3^D	0.020	0.029
NaCl	0.26–1	open	5	0.008	0.008	3^E	0.025	0.020
$NaHCO_3$	0.2–0.75	open	4	0.018	0.017	3^F	0.029	0.029
HCl	0–1	cell	5	0.002	0.002	3^G	0.004	0.004

analytical wavenumbers (cm^{-1}) selected in MLR

A	5346.7	5501.0	6110.5	7144.3
B	5315.8	5508.7	5794.2	
C	5346.7	8841.7		
D	5508.7	5963.9	6527.1	
E	5354.4	5454.7	5925.3	
F	5346.7	5871.3	5979.3	
G	5346.7	5423.8	8741.4	

[a] Concentrations calculated by PCR and MLR. [b] Number of eigenvectors indicated in PCR. [c] Number of analytical wavenumbers selected in MLR.

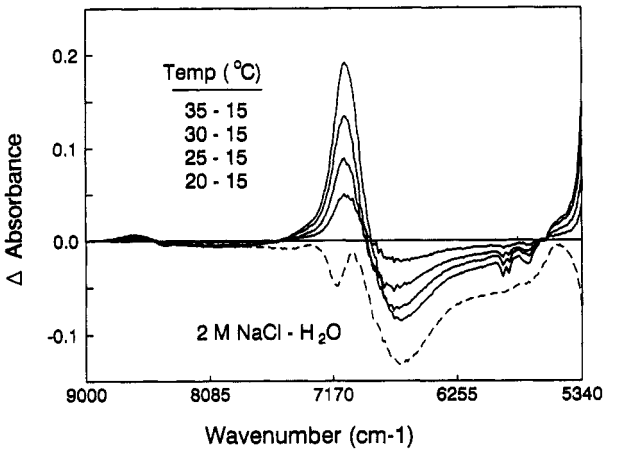

Figure 6. Difference spectra of water and NaCl solution measured with an open type of probe. Spectra in solid curves are difference spectra of water at 35, 30, 25, and 20 °C with the spectrum at 15 °C as reference. Spectrum in dashed curve is the difference spectrum of 2 M NaCl minus water at 15 °C.

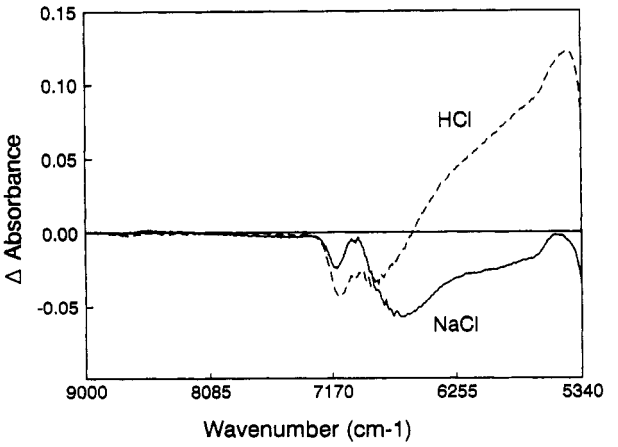

Figure 7. Difference spectra of 1 M NaCl and HCl solutions minus water, measured with a cell type of probe.

we explored the possibility of simultaneous measurement of electrolyte and temperature in aqueous solutions.

Near-IR spectra of NaCl solutions (0–2.031 M at increments of about 0.25 M) were measured at five temperatures (14.8–34.8 °C at increments of about 5 °C). The difference spectra of water at different temperatures (with water at 14.8 °C as

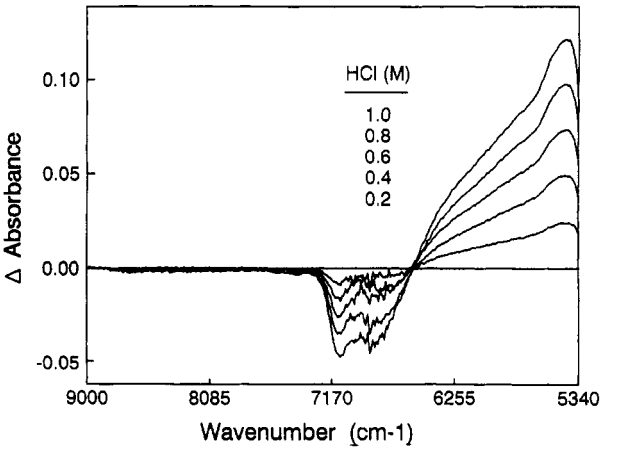

Figure 8. Difference spectra of HCl solutions minus water, measured with a cell type of probe.

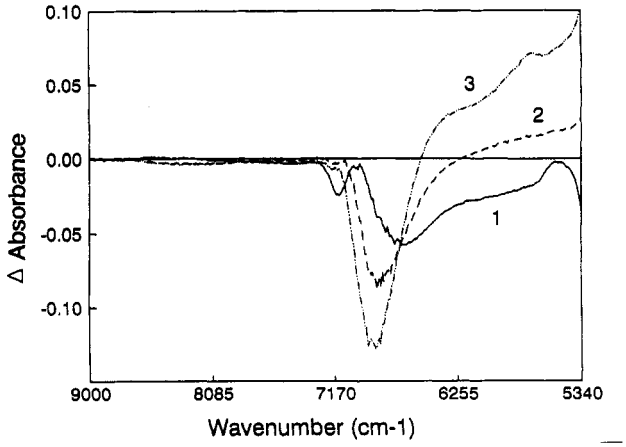

Figure 9. Difference spectra of 0.7 M NaCl, $NaHCO_3$, and Na_2CO_3 solutions minus water, measured with a cell type of probe: (1) NaCl; (2) $NaHCO_3$; (3) Na_2CO_3.

reference) are compared to that of 2 M NaCl solution minus water in Figure 6. The concentrations of NaCl and temperature were calculated by PCR, using five eigenvectors. The SEP's obtained are 0.015 M for NaCl and 0.40 °C for temperature. The NaCl concentrations and temperature were also calculated by MLR; four wavenumbers were needed for NaCl and seven for temperature. The SEP's produced are 0.023 M for NaCl and 0.55 °C for temperature.

Table II. Results for Multicomponent Measurements[a]

NaCl–Temperature (0–2.031 M, 14.8–34.8 °C)

	NaCl			temperature		
	n	SEE	SEP	n	SEE	SEP
PCR	5	0.017	0.015	5	0.42	0.40
MLR	4	0.024	0.023	7	0.47	0.55
LR_{iso}		0.064	0.069			

WN's NaCl: 5346.7, 5477.8, 5994.8, 8857.1
temp: 5879.0, 6743.1, 6758.6, 6766.3, 6874.3, 6882.0, 7221.5

NaCl–HCl (0–1 M)

	NaCl			HCl		
	n	SEE	SEP	*n*	SEE	SEP
PCR	5	0.009	0.010	5	0.004	0.004
MLR	4	0.034	0.039	4	0.006	0.007
LR_{iso}		0.021	0.023			

WN's NaCl: 6689.1, 7167.5, 8317.0, 8787.7
HCl: 5524.1, 5609.0, 7152.0, 8780.0

NaCl–$NaHCO_3$–Na_2CO_3 (0–0.7 M)

	NaCl			$NaHCO_3$			Na_2CO_3		
	n	SEE	SEP	*n*	SEE	SEP	*n*	SEE	SEP
PCR	6	0.008	0.008	6	0.012	0.012	6	0.005	0.005
MLR	3	0.022	0.022	3	0.012	0.014	4	0.016	0.015

WN's NaCl: 5501.0, 5624.4, 5639.9
$NaHCO_3$: 5362.1, 5470.1, 5902.2
Na_2CO_3: 5346.7, 5470.1, 8463.6, 8926.5

[a] Concentrations and temperature calculated by PCR, MLR, and LR_{iso}. *n* is number of eigenvectors or wavenumbers in PCR or MLR. WN's are analytical wavenumbers selected in MLR.

As seen in Figure 6, temperature does not affect the absorbance at 5601 cm^{-1} (isosbestic point). Thus, the absorbances at this wavenumber can be used to calculate the concentration of NaCl by linear regression (LR_{iso}). A SEP of 0.069 M is obtained for NaCl. This error, although significantly larger than that obtained by PCR and MLR, is only 3.7% of the full concentration range. This may still be very acceptable under certain experimental conditions.

Simultaneous Measurement of NaCl and HCl. The concentrations of NaCl and HCl in aqueous solutions were measured simultaneously. Thirty-six standard solutions were prepared according a two dimension matrix (6 × 6). The concentrations of both electrolytes ranged from 0 to 1 M at an increment of 0.2 M. The difference spectra of NaCl and HCl solutions minus water are shown in Figure 7. The concentrations were calculated by PCR and five eigenvectors were indicated. The SEP's obtained are 0.010 M for NaCl and 0.004 M for HCl. The concentrations were also calculated by MLR; four wavenumbers were needed for both NaCl and HCl. The SEP's produced are 0.039 and 0.007 M for NaCl and HCl, respectively. It can be seen (in Figure 7) that HCl which has larger perturbations than NaCl gives a smaller SEP.

The perturbations of HCl are zero at 6581.1 cm^{-1} (isosbestic point) as seen in Figure 8, and the absorbances at this wavenumber can be used to calculate the concentration of NaCl by linear regression (LR_{iso}). A SEP of 0.023 M is obtained for NaCl; this is smaller than that produced by MLR with four analytical wavenumbers. This result may be attributed to the facts that the perturbations by NaCl at the isosbestic point for HCl are very close to their maximum and that in the LR_{iso} calculation the spectra are baseline zeroed at 9000 cm^{-1}.

Simultaneous Measurement of NaCl, $NaHCO_3$, and Na_2CO_3. The concentrations of NaCl, $NaHCO_3$, and Na_2CO_3 in aqueous solutions were measured simultaneously. Thirty-six mixtures were prepared according to a ternary concentration matrix in which each electrolyte had concentrations of 0–0.7 M in 0.1 M increment. The difference spectra are shown in Figure 9. The concentrations were calculated by PCR using entire spectra, and six eigenvectors were indicated. SEP's of 0.008 M for NaCl, 0.012 M for $NaHCO_3$, and 0.005 M for Na_2CO_3 were obtained. Again, we find (from Figure 9) the trend that Na_2CO_3 which has the largest perturbations gives the smallest SEP.

The concentrations were also calculated by MLR, three wavenumbers were needed for NaCl and $NaHCO_3$, and four for Na_2CO_3. SEP's of 0.022 M for NaCl, 0.014 M for $NaHCO_3$, and 0.015 M for Na_2CO_3 were obtained. SEP for $NaHCO_3$ obtained by MLR is smaller than those for NaCl and Na_2CO_3; this is contrary to the sequence obtained by PCR. The results for all the multicomponent measurements are summarized in Table II.

CONCLUSIONS

In this paper, we discussed fiber-optic probes based on the perturbations of electrolytes on near-IR spectrum of water. These probes are universal and can be used to measure all electrolytes which cause perturbations to the water band. The probes are very simple, readily fabricated, and very inexpensive. Moreover, they can be used in the remote sensing of electrolytes in aqueous solution, especially in hostile environments. Different types of probes have been developed, and can be employed in different situations in process control.

Single or simultaneous measurements of electrolytes are possible with the fiber-optic probes developed in this study. Temperature and electrolytes can also be determined simultaneously. The concentrations of electrolytes can be calculated by linear regression using the absorbances at one selected wavenumber or at the isosbestic wavenumber of a component (LR and LR_{iso}), by multilinear regression (MLR) using the

absorbances at several selected wavenumbers, or by principal component regression (PCR) using entire spectra. In PCR, only one set of eigenvectors are used to calculate the concentrations of all electrolytes (and temperature) in a system. In MLR, however, different sets of wavenumbers are selected for the calculation of different components. Therefore, it is not surprising to see that the numbers of eigenvectors and wavenumbers in PCR and MLR are different. It is interesting to find that the numbers of wavenumbers in MLR for different electrolytes in a mixture are sometimes different (e.g., in the $NaCl–NaHCO_3–Na_2CO_3$ system). PCR gives the smallest SEP's for all of the measurements. SEP's obtained by MLR were smaller than those obtained by LR_{iso}, with one exception (i.e. NaCl in NaCl–temperature system). Although LR_{iso} gives the largest SEP's, it provides the basis for the simplest measurements with resonably good results. Standard errors of concentrations less than 10 mM are obtainable by PCR and MLR for concentrations in the range from 0 to 1 M.

In a laboratory, it is not difficult to scan the entire spectrum and PCR can be performed to achieve the smallest SEP. In process control, where real time monitoring may be required, the absorbances at selected wavenumbers can be measured and used to calculate concentration by linear or multilinear regression. For the latter measurements, a simple device can be developed using diode lasers or light-emitting diodes as the sources and photodiodes as the detectors to replace the expensive FT-near-IR spectrometer.

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