

Qualitative Analysis and Structural Confirmation of Several Surfactants by FT-Raman and FT-IR Spectroscopies

J.C. Bowman, Nicolet Spectroscopy Research Center, Madison WI / D.P. DeSalvo, Stepan Co., Northfield, IL

KEYWORDS

FT-IR, FT-Raman, detergents, cosmetics, personal products, surfactants

INTRODUCTION

Surfactants are used in numerous industries from household detergents and cosmetic products to industrial lubricants and enhanced oil recovery. Analysis of these materials has become of major importance to the end users as well as surfactant producers.

Since the advent of attenuated total reflectance (ATR) techniques, Fourier Transform infrared (FT-IR) has become a popular tool for the analysis of these aqueous materials because there is no sample modification. Another viable tool available to the analytical chemist in these industries is FT-Raman.¹ This technique is exciting and promising, yet relatively unexplored. Most analytical chemists have not yet had the opportunity to combine the complimentary results² from FT-IR and FT-Raman experiments in the analysis of the samples they typically encounter. Whereas absorptions in the infrared spectrum are due to the sample's interaction with the infrared beam causing a change in the dipole moment of the bond, the Raman effect is due to a change in the "polarizability" of the bond.³ Thus, bonds that are very polar are more likely to produce infrared active absorptions. Conversely, non-polar bonds are more likely to produce Raman active emissions. The O-H bands of water for example, are very weak (virtually non-existent) in the FT-Raman, but are frequently totally absorbing in the mid-IR. Furthermore,

since water is a very weak Raman scatterer, it does not contribute significant solvent effects or band broadening (as it does in the mid-IR spectrum) facilitating more effective spectral subtractions, quantitative analysis or other spectral manipulations. Therefore, many detergent solutions can be analyzed without sample preparation.

Another very important aspect of the near infrared FT-Raman approach is the energy of the excitation source – a Nd:YAG laser (1064 nm). The excitation energy is in a range where fluorescence due to electronic transitions does not occur as is often the case in the dispersive experiment. The energy of the argon ion laser (514 nm) normally used in the dispersive experiment is so high (in order to obtain useful signal-to-noise spectra) that fluorescence typically plagues the dispersive Raman experiment unless special precautions are taken. Because of this, the use of the Nd:YAG laser in the FT-Raman experiment virtually eliminates the need for "bleaching" the sample under the argon ion laser for many hours, use of special non-fluorescing glass sample holders and/or tedious glassware cleaning procedures.⁴

In addition, the FT-Raman technique is a higher throughput experiment than is the traditional dispersive Raman technique.⁵ It capitalizes on the ability to signal average many more scans in a much shorter period of time in order to quickly collect high signal-to-noise spectra. In fact, the FT-Raman technique has become sufficiently routine, and has been shown (under properly controlled conditions) to be very useful for quantitative analysis.⁶ Furthermore, the technique is applicable to many fields of

chemical analysis from amino acids to blended gasolines to fats and oils.^{7,8,9}

Since the introduction of the Magna-IR[®] 760 FT-IR spectrometer, spectral region changes are fast (less than 1 minute), routine and reliable. Implementation of dynamic alignment allows the interferometer to be optimized for both the less demanding mid-IR experiment as well as the far more challenging near infrared FT-Raman experiment using one optical bench and computer. This is an important bonus due to the complimentary nature of these two techniques.

Nicolet has recently introduced the Raman 950 System. It is the world's first completely dedicated and optimized FT-Raman system. Both systems provide excellent FT-Raman data. The Magna-IR 760 can have the FT-Raman capability added as an accessory for labs where both the FT-IR and FT-Raman techniques are important analytical tools. The Raman 950 System is generally intended for labs where the FT-Raman would be an important addition, but where an existing FT-IR is already present. It is designed to be easy to use as a routine analytical tool for a wide variety of samples found in both academic research and industrial analytical labs.

The purpose of this application note is to demonstrate the usefulness and complimentary nature of the results obtained from both the FT-IR and FT-Raman techniques in the qualitative analysis of surfactants. A survey sampling of several standard surfactants were chosen: anionics (alcohol sulfate and linear alkylbenzene sulfonate), nonionics (alcohol ether, amide, and ethoxylated nonylphenol, linear alkylbenzene feedstock), and quaternaries (both aryl and aliphatic).

These samples were chosen as being characteristic of many typical surfactants. All samples were provided by Stepan Co. of Northfield, Illinois.

EXPERIMENTAL DETAILS

All spectra were acquired using a Nicolet Magna-IR 760 equipped with a standard Nicolet FT-Raman module. The system was configured for near infrared FT-Raman using a Raman optimized CaF_2 beamsplitter. The standard air-cooled 2W Nd:YAG laser emitting at 1064 nm was used as the excitation source. The FT-Raman data were collected with 1.25 watts of excitation energy in an NMR tube using the standard 180° reflective backscattering sampling/collection geometry. This arrangement employs a very fast $f/0.4$ mirror providing a wide 130° field of view for optimal collection and collimation of the scattered radiation. FT-Raman data were collected using 4 cm^{-1} resolution and 100 scans (about 3 minutes).

The FT-Raman spectra were all normalized to white light (corrected for the emissivity curve of the black body at its known temperature of 1925K). The procedure normalizes the band intensities for the effects of detector sensitivity and instrument filter function versus wavelength. This is analogous to removing the instrument background by performing a ratio of the sample's single beam spectrum divided by the background single beam spectrum in conventional FT-IR. The procedure is considered essential for both repeatable qualitative and quantitative Raman analysis. White light correction is an integrated, standard of both the Magna-IR and Raman 950 designs. The Magna-IR 760 was then quickly switched over (less than 1 minute) from near infrared FT-Raman to mid-IR. The infrared data was obtained using an out of the compartment trough plate horizontal ATR equipped with a ZnSe crystal (45° angle of incidence) in the main bench sample compartment. Mid-IR spectra were acquired using a Ge on KBr beamsplitter, DTGS detector and a global source. The mid-IR data were collected at 4 cm^{-1} using 64 scans (less than 1 minute).

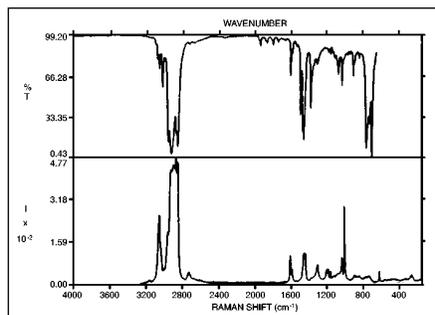


Figure 1: Linear Dodecylalkylbenzene Feedstock

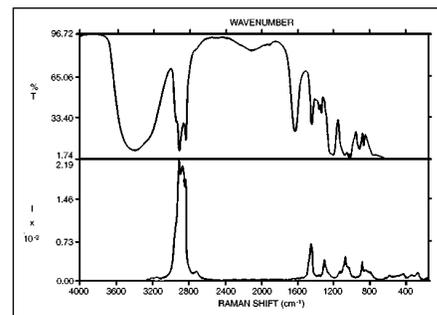


Figure 6: Sodium Ethoxylated Lauryl Alcohol Sulfate -30% (average 3 moles ethylene oxide per molecule)

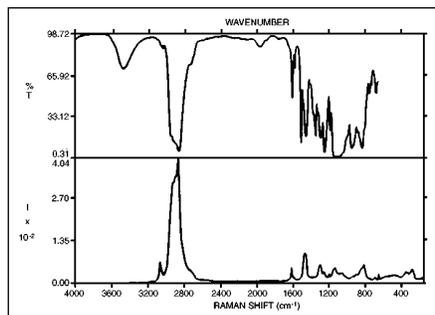


Figure 2: Ethoxylated Nonylphenol (average 12 moles ethylene oxide per molecule)

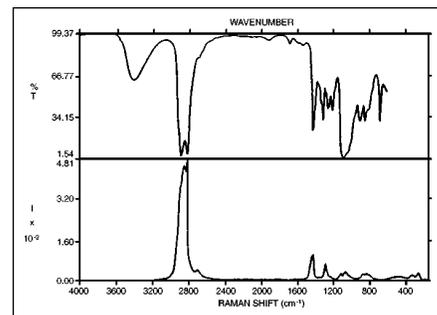


Figure 7: Ethoxylated Lauryl Alcohol Feedstock (average 3 moles ethylene oxide per molecule)

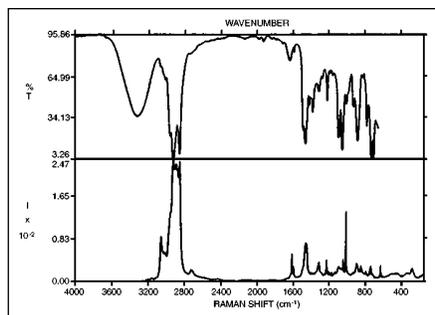


Figure 3: Dimethyldiphenylammonium Chloride

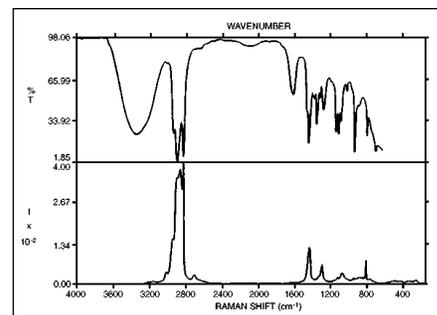


Figure 8: Dimethylditalowammonium Chloride

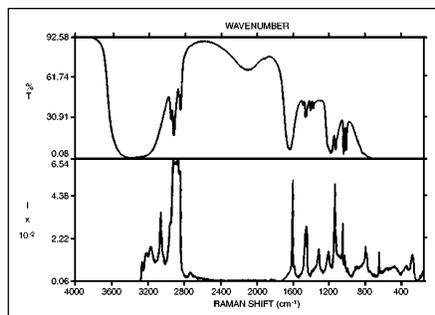


Figure 4: Sodium Linear Alkylbenzene Sulfonate -40%

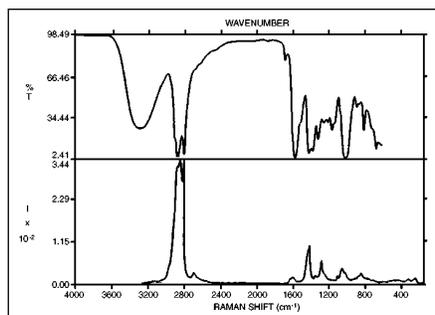


Figure 5: Diethanolamide

RESULTS AND DISCUSSION

The data in Figures 1-8 are the spectral plots of the horizontal ATR transmission spectra (on top) compared to the Raman shifted spectra (on bottom). They all show several interesting features. A few of the more general features will be highlighted first followed by a more in depth analysis of the sample of sodium linear alkylbenzene sulfonate at 40% in water (Figure 4). These are common raw material concentrations for many formulator and consumer products companies.

First of all, notice several of the similarities. Bonds that are mildly polar or hydrogen bonded and/or somewhat polarizable appear in both the FT-Raman spectrum and the mid-IR spectrum as well. For example, the aliphatic C-H stretches $3000\text{-}2800 \text{ cm}^{-1}$ appear clearly

in Figures 1-8. The aromatic C-H stretch ($3100-3000\text{ cm}^{-1}$) can also be seen in both the FT-IR and the FT-Raman spectra in Figures 1-3, although it is more prominent in the FT-Raman. In sodium linear alkylbenzene sulfonate (Figure 4) these bands are completely obscured in the FT-IR spectrum due to the O-H stretch from the water present. Also note the C=C stretch near 1600 cm^{-1} in Figures 1-4 is significantly more prominent in the FT-Raman spectra than in the mid-IR. Furthermore, the sharp features near 3100 cm^{-1} in the FT-Raman spectra from Figures 1-4 easily confirms that this C=C bond is in fact aromatic in nature – which is not quite as obvious in the mid-IR spectra. Such a confirmation is frequently much more difficult by using only the mid-IR technique when the product is a blend of aromatic hydrotypes, other surfactants and water.

Conversely, note several of the striking differences between the mid-infrared and FT-Raman data. For example, very polar bonds such as the O-H stretch ($3400-3100\text{ cm}^{-1}$) which are very strong in the mid-IR do not appear in the near infrared FT-Raman spectra (see Figures 2-8). Figure 5 shows the amide carbonyl has a very small absorbance in the FT-Raman spectrum, but very prominent in the mid-IR (1620 cm^{-1}). Furthermore, the C-O-C ether stretch (near 1125 cm^{-1}) appears very strong in the mid-IR spectra (see Figures 2, 5-7) but rather weak in their respective FT-Raman spectra.

Compare Figures 3 and 8. Notice that the sharp band near 800 cm^{-1} in the FT-Raman spectrum in Figure 8 is difficult to distinguish in the FT-Raman spectrum from Figure 3. Although both compounds are quaternary surfactants, the material in Figure 3 has at least one aromatic functional group on the molecule (as noted above in discussion the C=C stretch), and the material from Figure 8 does not. Features such as these can be used to very easily differentiate which type of quaternary surfactant is the predominant species by combining and comparing both the Raman and infrared data.

The above analysis makes some general observations in comparing FT-IR data and FT-Raman data. A closer look at the data from the sample sodium linear alkylbenzene sulfonate (Figure 4) reveals some very

useful interpretive information and demonstrates why mid-IR analysis only reveals a portion of the story. First of all, recall that horizontal ATR is the fastest and easiest technique for analyzing aqueous samples by FT-IR because the sample can be analyzed neat. However, notice the very strong water absorption bands (centered at 3300 cm^{-1} , 2120 cm^{-1} and 1650 cm^{-1}) in the FT-IR spectrum of Figure 4, which obscure a significant portion of the carbonyl region ($1750-1600\text{ cm}^{-1}$), the C=C stretching region ($1650-1500\text{ cm}^{-1}$) and the O-H/N-H stretching region (3300 cm^{-1}). Because of the intensity of the O-H stretch there is very little, if any, evidence that the material has significant aromatic content due to the lack of aromatic C-H stretching between $3100-3000\text{ cm}^{-1}$. Furthermore, since much of the carbonyl and C=C regions are also obscured, even if this sample had been suspected of being aromatic, no substitution pattern can be gleaned in the $2100-1600\text{ cm}^{-1}$ area. About the only hint that this material is aromatic, is the small doublet near 1050 cm^{-1} ; but no confirmational evidence can be seen. The only obvious information available from the mid-IR data is the appearance of the sulfonate band near 1200 cm^{-1} . In order to obtain a truly useful FT-IR spectrum from this material, the water must be dried off, a rather tedious process. One could, in theory, simply perform a spectral subtraction to remove the water. However, due to the hydrogen bonding and subsequent band broadening (because FT-IR responds to the change in the dipole moment) in polar solutions such as this, water subtractions of heavily hydrogen bonded samples frequently result in small peak shifts and therefore, negative or derivative shaped spectral artifacts. This again makes interpretation very difficult.

In comparison, the FT-Raman data shown in Figure 4 does not suffer from any of these inherent difficulties. First, notice that the water bands are nonexistent – and this sample was run as received consisting of nearly 60% water! Second, the aromaticity is readily apparent. This is easily seen near 3100 cm^{-1} and the strong C=C band which occurs near 1650 cm^{-1} . Substitution information can also be ascertained by the pattern near 3100 cm^{-1} . This can be

accomplished by comparing this plot to the FT-Raman data in Figure 1. The linear dodecylalkylbenzene (Figure 1) shows only one band in this region and it is known to be singly substituted. Confirmation of this can be seen by the presence of the small band near 620 cm^{-1} . It is due to the presence of a para-disubstituted benzene ring.² This band normally shifts to between 650 and 630 cm^{-1} in the case of the mono-substituted compound. Thus, the material in Figure 4 could not be a singly substituted ring (as is the material in Figure 1) and therefore must be a multiply substituted aromatic species. Presuming the sample is not a mixture of compounds, and that we already know the material contains aliphatic C-H (or at least one alkyl group) due to the C-H stretch ($2900-3000\text{ cm}^{-1}$), and since the alkyl functionality is known to be a para “director” activating group toward other possible substituents, we can reasonably conclude from the data in Figure 4 that the preponderance of this material is a para-disubstituted alkylated benzene sulfonate. This conclusion could not have easily been reached without the FT-Raman data. This clearly demonstrates the need for both types of spectral data in analyzing various surfactants.

CONCLUSIONS

It can be seen from the data presented above, that combining results from both the FT-IR and FT-Raman techniques from the same sample provides useful structural information that neither alone can completely provide. This demonstrates the need for both types of spectral data in analyzing various surfactants. Compound identifications and spectral subtractions from mixtures of these compounds would also be expected to aid the analytical chemist in the analysis of blended surfactants using these two techniques. The data shown here may have implications in the determination of the number of moles of ethylene and propylene oxide units per molecule of ethoxylated nonionic surfactants. It may also be possible to analyze quaternary and anionic surfactants in much greater detail, either qualitatively or quantitatively. For the purpose of surveying various samples in this application note we

have only scratched the surface of the FT-Raman technique's potential in this field of chemistry. It may even begin to revolutionize the analysis of these types of compounds because the analyst can now obtain useful structural information regarding the less polar bonds in the sample – something FT-IR alone can not provide.

REFERENCES

1. Hendra, P., Jones, C., Warnes, G., *Fourier Transform Raman Spectroscopy, Instrumentation and Chemical Applications*, (Ellis Horwood: London, UK), 1991.
2. Lin-Vien, *et al.*, *The Handbook of Infrared and Raman Characteristics Frequencies of Organic Molecules*, (Academic Press, Inc.: Boston, MA), 1991.
3. Banwell, C.N., *Fundamentals of Molecular Spectroscopy, 3rd ed.*, (McGraw Hill: London, UK), 1972.
4. Hirschfeld, T., Chase, B., *Applied Spectroscopy*, **40**, 133, 1986.
5. Jacquinet, P., *Rep Prog Physics*, **23**, 267, 1960.
6. Smith, M., Walder, E., "Quantitative Analysis Using FT-Raman Spectroscopy," *Nicolet Application Note no. 9145*, 1991.
7. Smith, M., Garry, M., "Structural Analysis of Amino Acids by FT-Raman and FT-IR Spectroscopy," *Nicolet Application Note no. 8928*, 1989.
8. Smith, M., Walder, E., Kemeny, G., "A Study of Blended Gasolines Using FT-Raman and FT-IR Spectroscopy," *Nicolet Application Note no. 9142*, 1991.
9. Petty, C., Garry, M., Walder, E., "Characterization of Fats with FT-Raman Spectroscopy," *Nicolet Application Note no. 9147*, 1991.

This application note is for informational purposes only. Nicolet Instrument Corporation makes no warranties, expressed or implied.

Magna-IR is a registered trademark of Nicolet Instrument Corporation.