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Fourier Transform Infrared and Raman Spectroscopic
Characterization of Homogeneous Solution Concentration Gradients
Near a Container Wall at Different Temperatures

By

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(NASA-CR-188541) FOURIER TRANSFORM INFRARED
AND RAMAN SPECTROSCOPIC CHARACTERIZATION OF
HOMOGENEOUS SOLUTION CONCENTRATION GRADIENTS
NEAR A CONTAINER WALL AT DIFFERENT
TEMPERATURES Final Technical Progress

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SUMMARY

Fourier transform infrared (FTIR) and Raman spectroscopic techniques have been used to study the solution concentration gradient in succinonitrile-rich and water-rich homogeneous solutions. The spectroscopic data shows significant concentration dependency. Although FTIR-attenuated total reflectance could not yield surface spectra since the evanescent infrared wave penetrated deep into the bulk solution, it showed that water-rich clusters were decreased at higher temperatures. This result is consistent with the calorimetric results reported earlier.

1. INTRODUCTION

Transparent binary metallic alloy models are important to material and metallurgical sciences because they permit visual observation of phase transformation and processes during solidification [1]. The succinonitrile-water solution is a well known model system for the non-ideal homogeneous and miscibility-gap type solutions and it serves as a model system for binary metallic alloys [2]. Frazier et al. [2] has demonstrated that a water-rich layer adjacent to a hydrophilic surface is present upon sectioning aqueous succinonitrile rich ingots which were fast-quenched through the miscibility gap. Fisher and Degennes [3] predicted that the concentrations in the immediate vicinity of a wall are perturbed by the wall over a distance on the order of a correlation length. Later, it was confirmed experimentally [4,5] that if a binary solution of the miscibility-gap type is cooled from above its consolute temperature while in the single phase region, critical adsorption of the phase having the highest chemical affinity for the container surface will occur. The implication is that a layer of the preferentially wetting phase exists near the wall immediately above the critical temperature.

In spite of these interesting observations, knowledge on the chemical nature of surface films on walls of opposite affinities for the aqueous minority phase is still lacking. Significant differences in solidification in hydrophilic and hydrophobic cells have been observed [6] which suggest that container surfaces play an important role in materials processing.

The present spectroscopic (Fourier transform infrared and

Raman) studies investigated the contribution of wall effects on composition shifts in the wall vicinity, and on solidification from a slightly hypo-monotectic solution. Our objective was to establish the extent to which preferred composition fluctuations in homogeneous miscibility-gap type solutions influence solidification behavior through wetting phenomena. Additionally, the spectroscopic information would supplement the differential scanning calorimetry (DSC) experiments performed on the fast-quenched succinonitrile-water solutions by Frazier and his coworkers at the Space Science Laboratory of the Marshall Space Flight Center.

In addition to the succinonitrile-water system, FTIR and Raman spectra were also made on HOD/H₂O and non-polar solvents such as benzene, ethylene glycol, etc. in order to study the extent of interaction of the succinonitrile molecule with the solvent and container surface.

2. EXPERIMENTAL

2.1 Chemicals

Succinonitrile (SCN, Eastman Kodak) was purified by vacuum distillation twice. 99.9+% benzene (HPLC grade, Aldrich) was used without further purification. Distilled water, filtered to 10 M cm resistivity was used to prepare samples.

2.2 Preparation of Solutions

2.2.1 Aqueous SCN solutions

SCN-H₂O

The SCN-water solutions for Fourier transform infrared-attenuated total reflection (FTIR-ATR) were prepared from double-

distilled SCN and double-distilled water. Molten SCN was mixed with water and allowed to equilibrate and separate into two clear phases in a water-jacketed separatory funnel and maintained at the selected temperature for at least 24 hours prior to analysis.

SCN-HOD-H₂O

The SCN-HOD/H₂O samples were prepared in a similar manner using a mixture of approximately 20% HOD and H₂O prepared by mixing D₂O with H₂O in approximately 1:10 volume ratio.

2.2.2 Non-aqueous SCN solutions

SCN-Benzene solution

The SCN-benzene solutions for FTIR-ATR analysis were prepared from SCN and benzene. Equilibrium solutions were prepared in a manner similar to aqueous solutions. Care had to be taken to prevent benzene evaporation during sample transfer. No loss of benzene from a benzene-SCN solution in the CIRCLE cell was observed over a period of more than 4 hours. Solutions for Raman analysis were prepared similarly to aqueous solutions and maintained at room temperature.

2.3 Spectroscopic measurements

2.3.1 Fourier transform infrared spectroscopy

All FTIR-ATR spectra were taken with a Mattson Sirius 1000 FTIR spectrophotometer equipped with a SpectroTech CIRCLE "open boat" ATR cell (Fig. 1) with a ZnSe ATR crystal and a TGS or HCT detector. The empty ATR cell was used as background. Transmission IR spectra of benzene-SCN solutions were taken in a sealed KBr cell with a 0.25 mm sample pathlength.

Initially, FTIR-ATR spectra were taken at room temperature

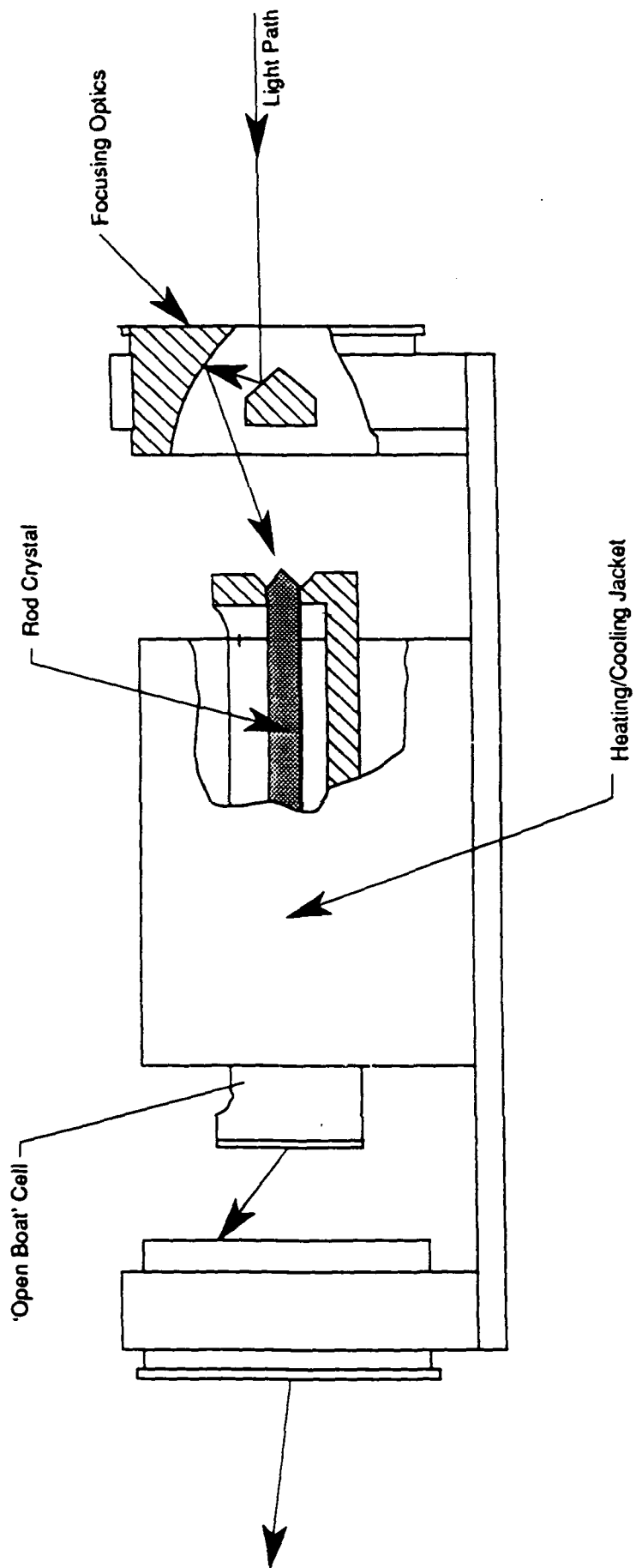


Fig. 1 The CIRCLE ATR cell with jacket

with no effort at precise temperature control. Later, all spectra were taken with a CIRCLE cell which was equipped with a heating/cooling jacket, through which water from a temperature control bath could be circulated. This arrangement allowed temperature control of better than 0.5°C over the range $15 - 55^{\circ}\text{C}$. The temperatures measured were actually the temperatures of the jacket surrounding the ATR cell. An aliquot of the phase to be analyzed was placed in the CIRCLE cell maintained at the equilibration temperature of that phase. Time was allowed for the system to come to thermal equilibrium and for water vapor and CO_2 to clear from the IR chamber, typically it took about 30 minutes. One or more spectra were then taken and the temperature of the bath changed. A spectrum was taken as soon as the jacket temperature had reached the specified temperature, and another a short time later. Selected samples were allowed to equilibrate for two hours, during which time spectra were taken at intervals. In most cases, no differences were observed among the spectra taken at the same temperature regardless of equilibration time.

2.3.2 Raman spectroscopy

The Raman spectra were taken using the macrochamber of an ISA MOLE/U1000 Raman spectrometer (Instruments, S. A.), equipped with a thermoelectrically cooled RCA 31034 photomultiplier tube detector. The 514.1 nm line of a Spectra Physics Series 2000 cw argon ion laser was used for excitation. Spectral resolution was 5 cm^{-1} .

For Raman spectra taken below room temperature, the sample was placed in a capillary tube which was mounted in a double walled glass cell through which vapors from liquid nitrogen were passed. This set up allowed spectra to be taken as low as -50°C (223 K).

3. RESULTS

3.1 Succinonitrile-Benzene System and the ATR Technique

Initial work was focused on establishing reliable analytical methods using the SCN-benzene system and ATR cell with a ZnSe crystal for surface FTIR spectroscopy. ZnSe in contact with the SCN-benzene system was chosen over quartz in contact with aqueous systems because, while both systems behave quite similarly, the ZnSe crystal has greater durability and a wider IR window over the region of interest. As we have shown by contact angle measurements, benzene exhibits preferential wetting of ZnSe (with contact angle of about 10 degrees, see Fig. 2) and hence may play a role in solidification from SCN-benzene systems similar to that played by hydrophilic surfaces in contact with aqueous systems.

Transmission and ATR spectra of several concentrations of SCN-benzene solutions were obtained using a ZnSe ATR crystal. Fig. 3 shows a spectrum of a 77% (w/w) SCN-benzene solution. The SCN peak locations correspond very closely to the published transmission data. The locations of most benzene peaks also correspond to published values. Exceptions are two benzene peaks which, in pure benzene spectra near their literature values of 1960 and 1815 cm^{-1} (ring overtones), but appear shifted toward higher wavenumbers with increasing SCN concentration. This

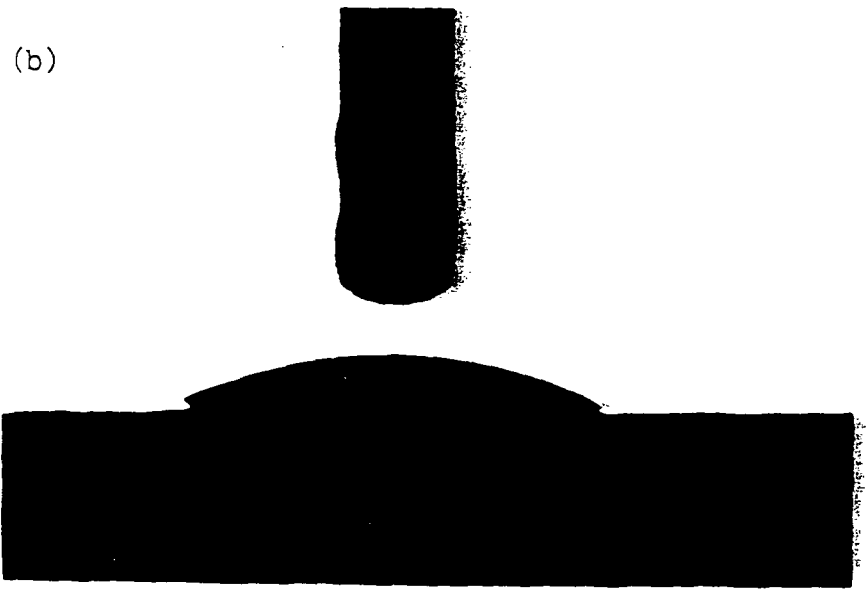
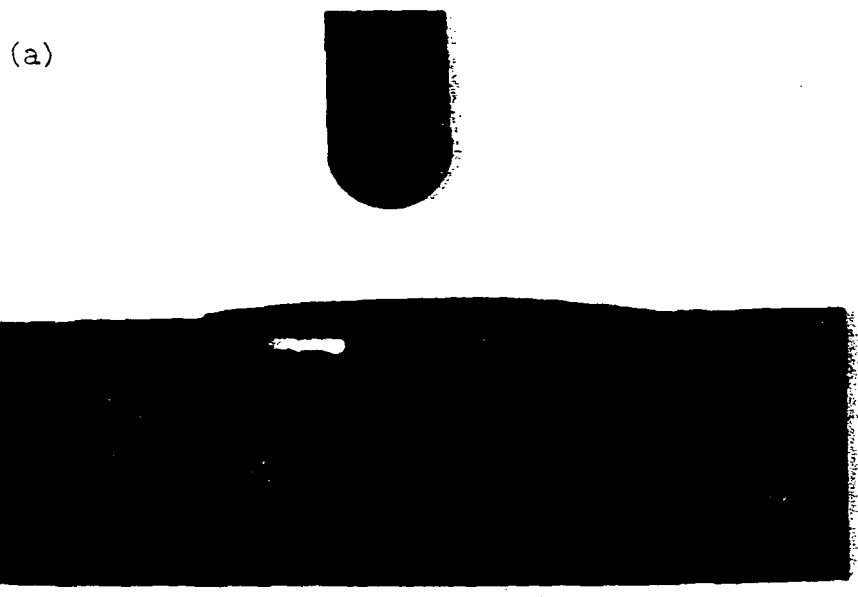


Figure 2 Contact angle with polycrystalline ZnSe surface
(a) Pure benzene (b) SCN-benzene solution

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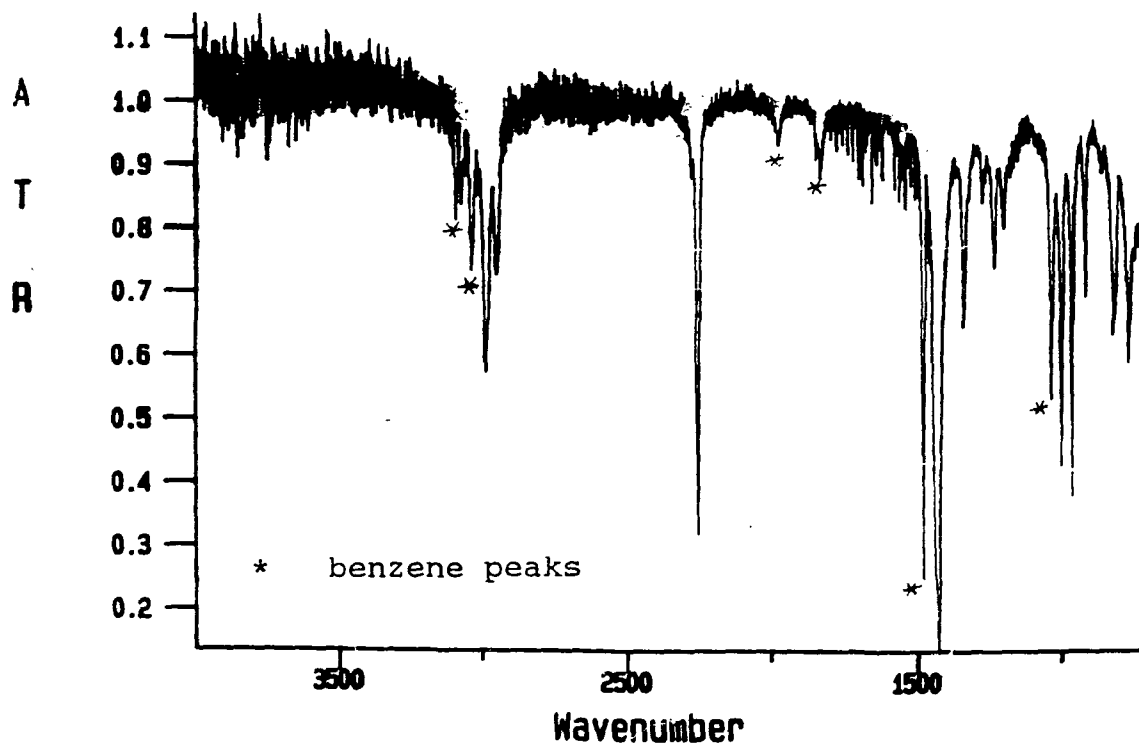


Figure 3 Attenuated total reflectance spectrum of 77% (w/w) succino-nitrile-benzene solution

effect is observed in both ATR and transmission spectra and thus cannot represent interaction of benzene with the ZnSe surface.

To investigate surface effects, we determined whether or not a layer existed near the ZnSe crystal during equilibration. Since the Gibbs surface excess is on the order of a few angstroms, and the calculated penetration depth [7] of the electromagnetic radiation into the bulk solution was about 2 μm (see Fig. 4), we concluded that the FTIR spectra observed is bulk phase. Furthermore, the thickness of any adsorbed film, if present, had to be less than the evanescent wave penetration depth since transmission spectra give identical spectra. Additionally, the effect of a species on the surface of the ATR crystal, i.e., any change in adsorption onto the crystal surface, should result in drastic changes in the spectrum. Therefore ATR spectra of pure benzene were taken at various temperatures ranging from 12°C to 35°C. No significant differences were noted among these spectra, indicating that no change in adsorption of benzene onto the surface occurred with change in temperature.

Next, a two phase benzene-SCN system was equilibrated at 12°C, and ATR spectra were taken at temperatures ranging from 12°C to 35°C. Again no significant differences were noted among these spectra. However, when the benzene-SCN system were allowed to equilibrate at 15°C, a sharp increase in the intensity of the benzene peaks and a concomitant decrease in the intensity of the SCN peaks occurred at about 13°C (Fig. 5). Examination of the ATR cell at this point revealed tiny particles on the surface of the ATR crystal, but the bulk solution appeared to remain clear. Since the solution should begin to separate into two phases

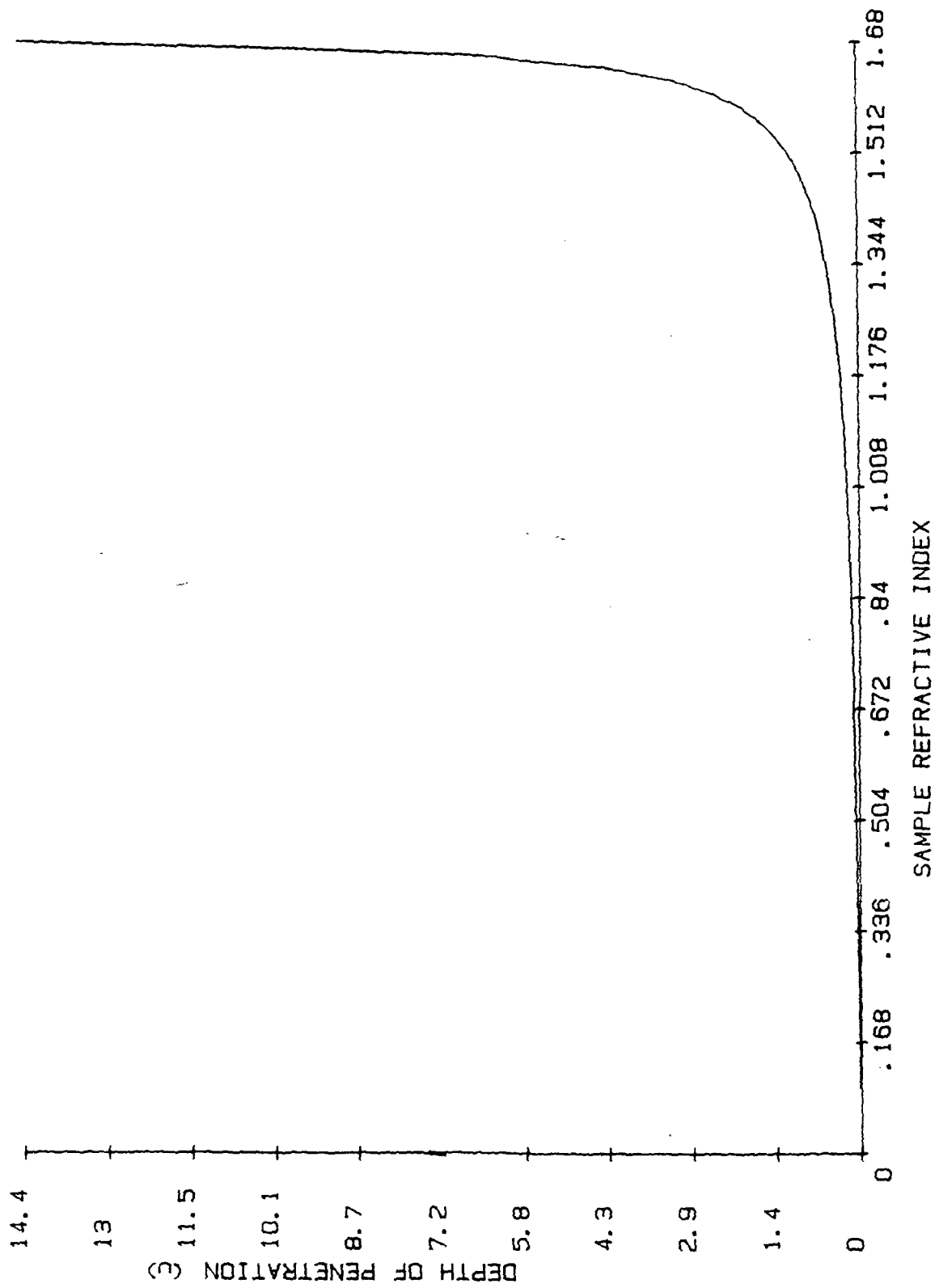


Fig. 4 Calculated effective depth of penetration
 $N_1 = 2.4$; Incidence = 45 deg; $Nu = 2250$

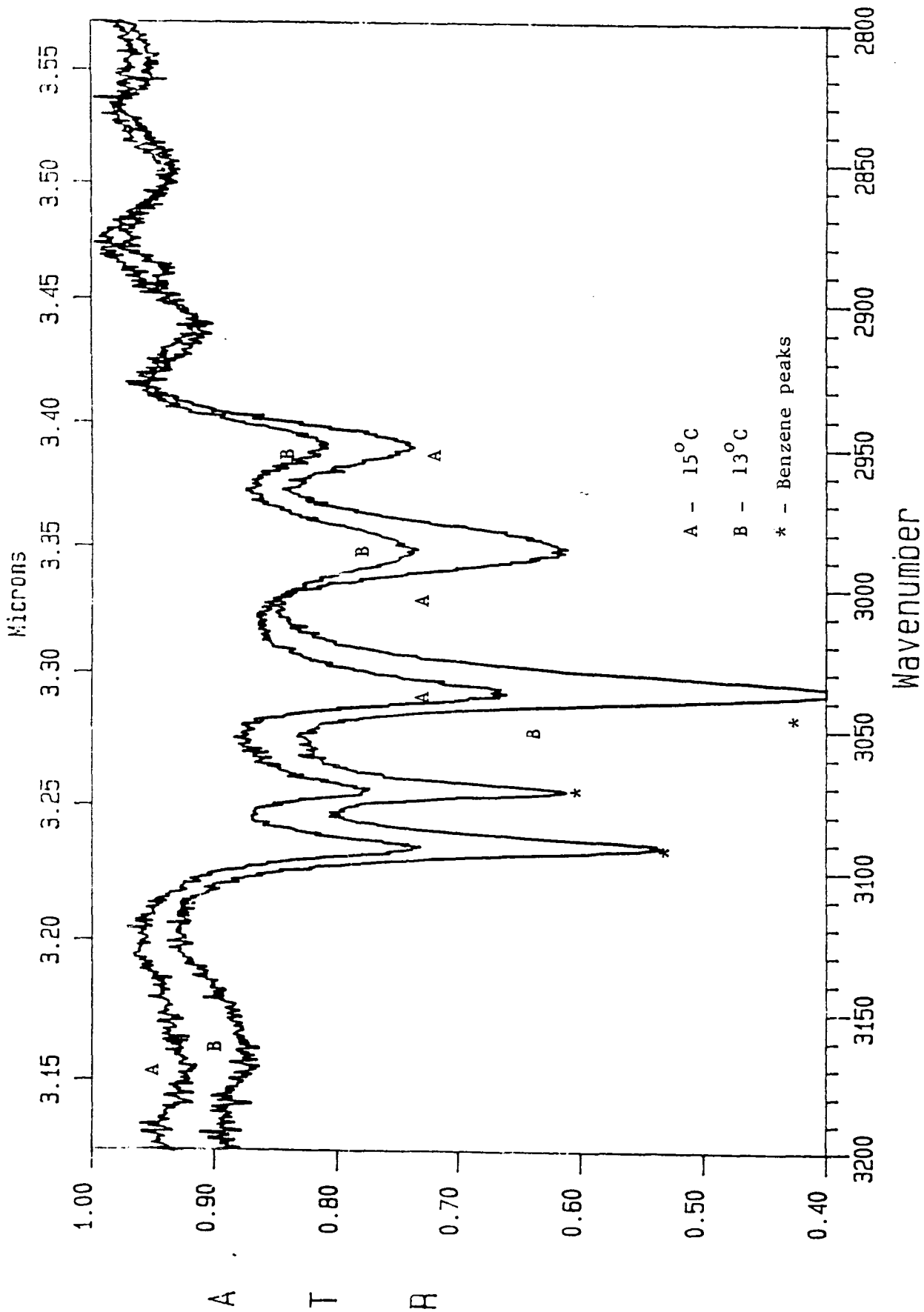


Fig. 5 The FTIR spectrum of the benzene-SCN system in the region $2800-3200\text{ cm}^{-1}$ at 13 and 15 °C

immediately below 15°C, it is not clear why the spectral change is not observed until about 13°C. It is possible that the loss of a small amount of benzene through evaporation may be responsible. A loss of benzene would lower the consolute temperature (see the phase diagram of SCN-benzene system in Fig. 6). Later, we found that succinonitrile reacted with benzene slowly. Hence, on the basis of these findings, we concentrate our study on the SCN-water system.

3.2 Succinonitrile-water system

After determining that spectra would be bulk-phase, we observed spectroscopic behavior of certain vibrational modes of the SCN-H₂O system, at different temperatures and compositions, to establish whether certain solution aggregates could contribute to solution dynamics. Presumably, if molecular interactions were strongly a function of temperature, one could infer the nature of preferred temperature dependent aggregates which may or may not be subject to adsorption on a hydrophilic surface.

In SCN-H₂O solution water-rich (or HOD/H₂O rich) phases, the nitrile stretching band, located at 2254 cm⁻¹ in the FTIR spectrum of liquid SCN, is shifted to higher frequency up to 6-8 cm⁻¹ (Fig. 7) with increasing water content. Raman spectra of these solutions (Fig. 8) and aqueous solutions of other dinitriles (e.g. glutaronitrile, adiponitrile, 1,6-dicyanohexane) show similar shifts in the nitrile stretching band. On the other hand, no such shift was observed in FTIR or Raman spectra of the SCN-rich phases (Fig. 9) or in either phase of benzene-, ethylene glycol-, CH₃OH-, or C₂H₅OH-SCN systems. This increase in

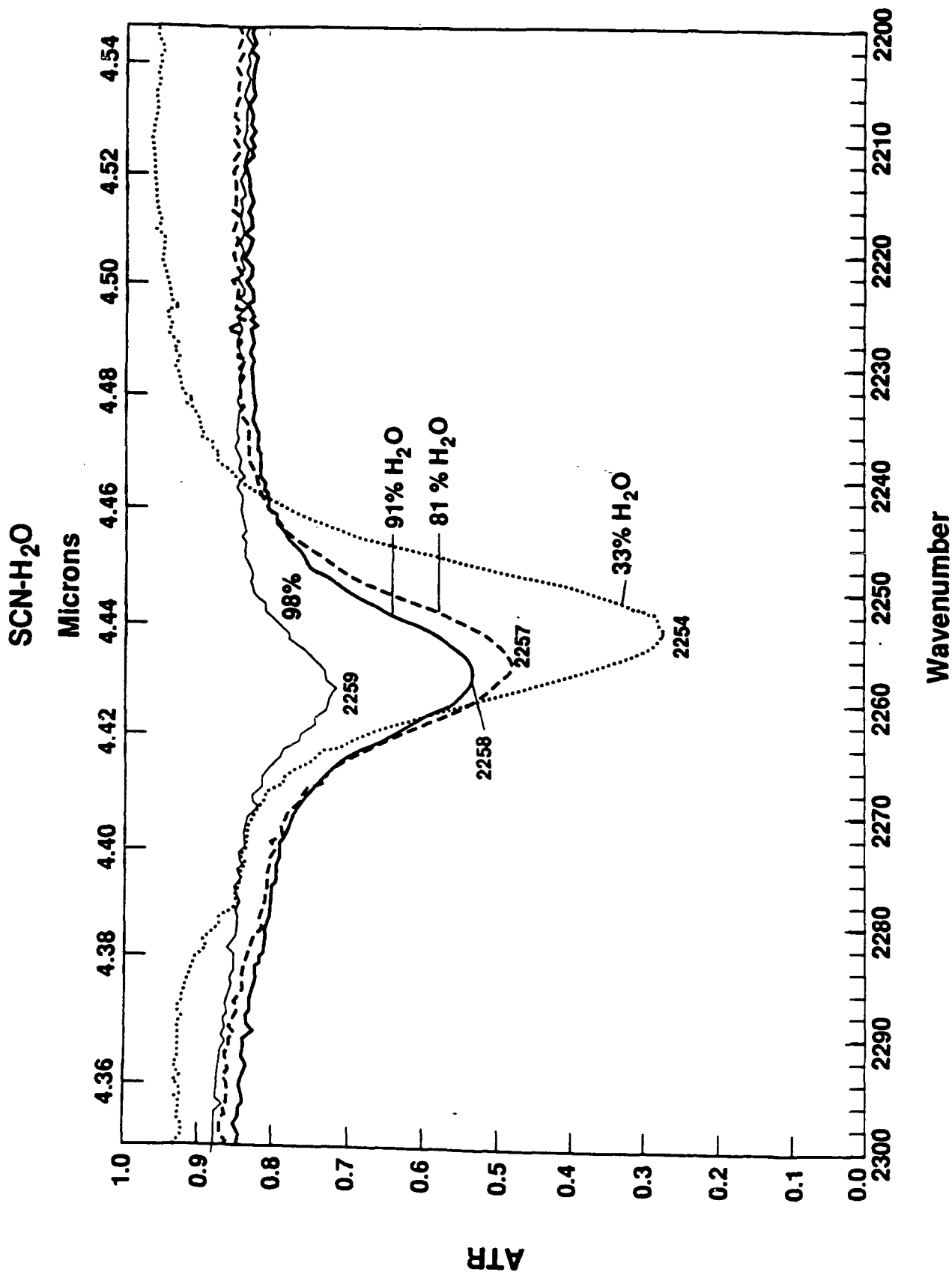


Fig. 7 Variation of the nitrile stretching band (IR) with water concentration at 60 °C

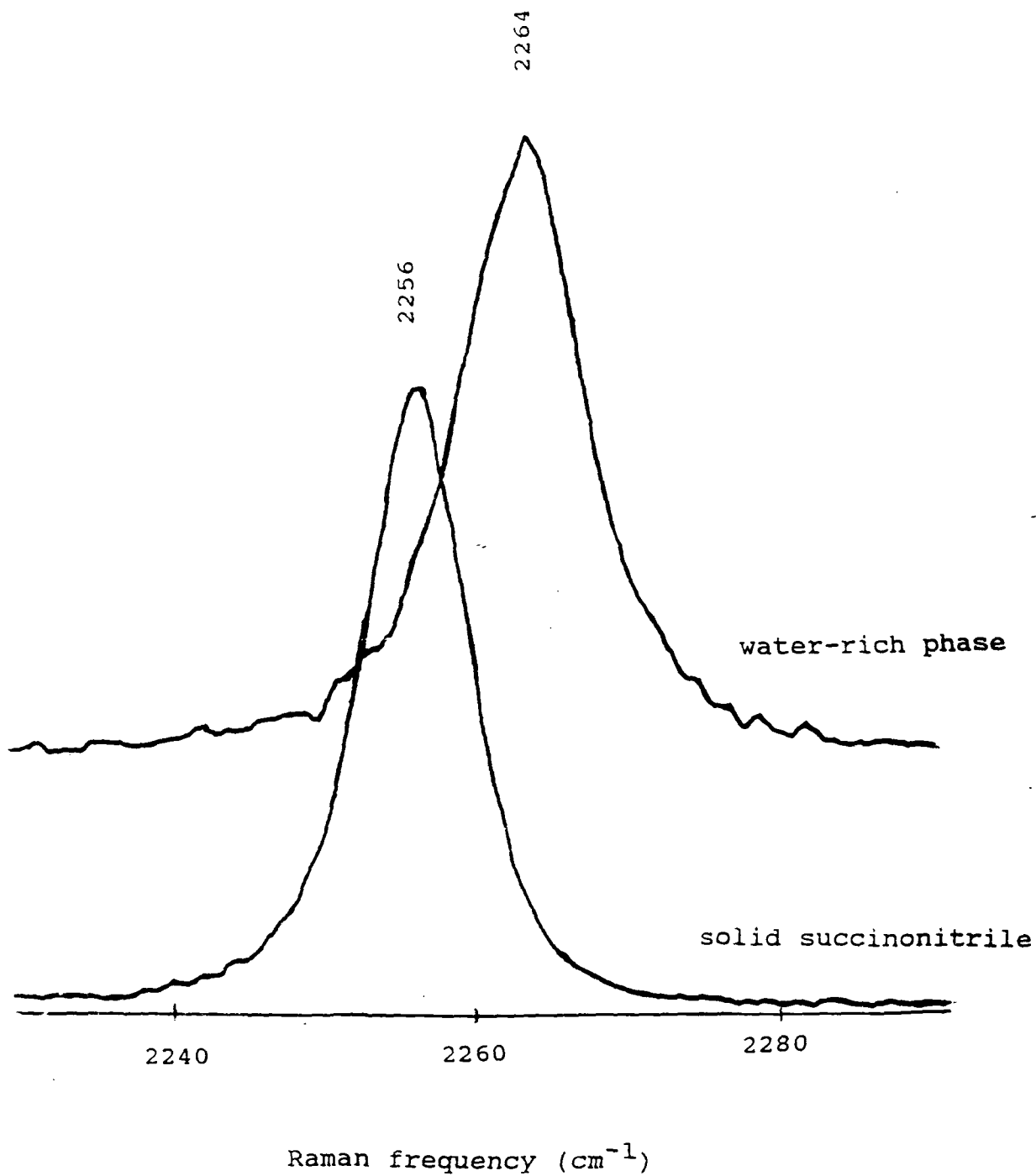


Fig. 8 The nitrile stretching band in the Raman spectra of the SCN-H₂O water-rich phase and solid succinonitrile

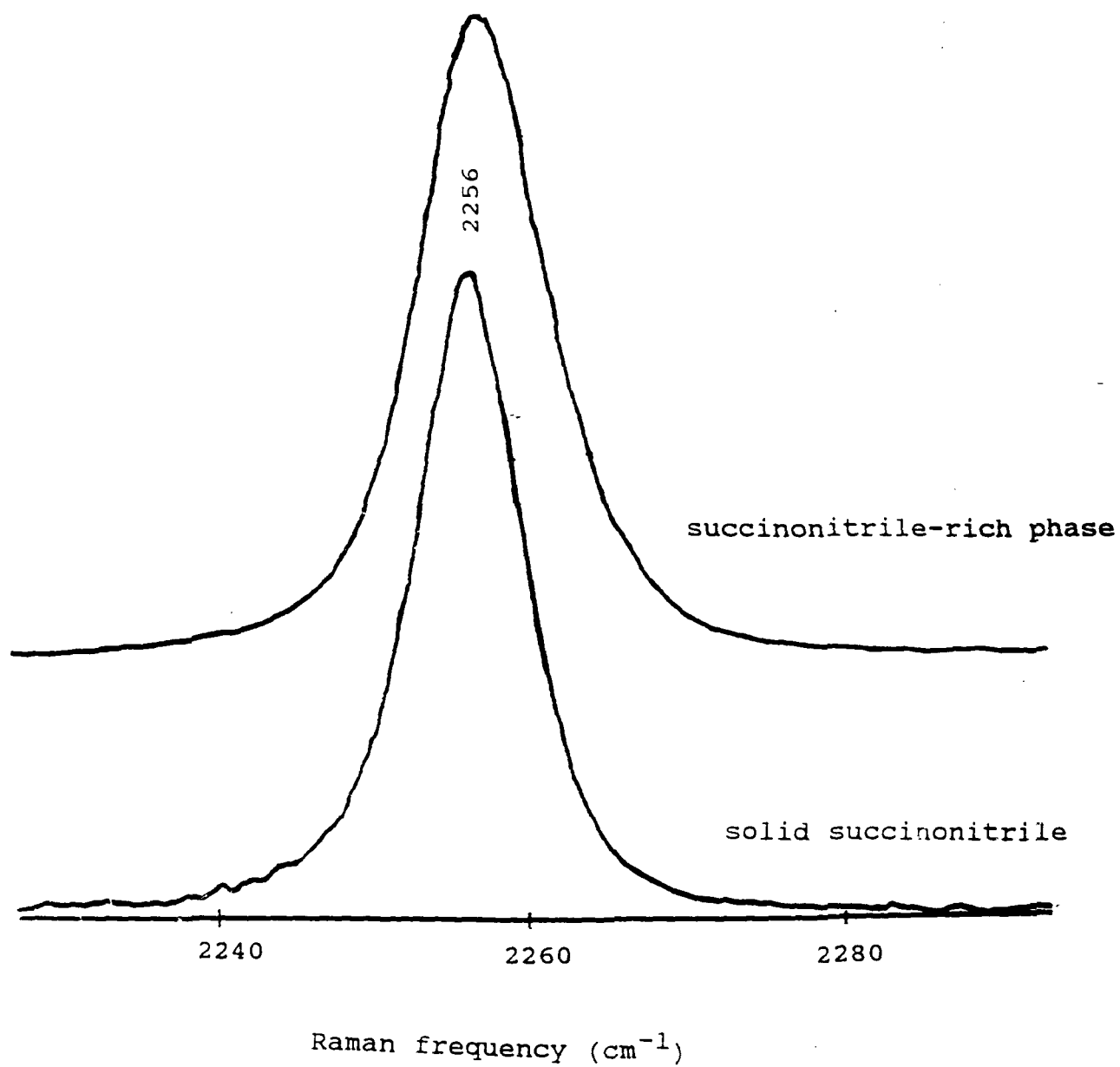


Fig. 9 The nitrile stretching band in the Raman spectra of the SCN-H₂O succinonitrile-rich phase and solid succinonitrile

stretching frequency of the CN group, as the water content is increased, is indicative of increasing hydrogen bonding of the SCN and the water molecules. If water concentration is increased (in the homogeneous region of the phase diagram, $T > 55$ °C, so that water concentration can be varied continuously) the nitrile peak shifts back toward 2254 cm^{-1} as water concentration is decreased. This represents a weakening of the SCN-water interactions.

In water-rich SCN-H₂O solutions, the OH stretching band of water (ca. 3550 cm^{-1}) exhibits a slight shift from its position in pure water. This shift is more clearly seen in the more narrow OD stretching band of HOD. The OH and OD bands of the SCN-rich phase are naturally much smaller, reflecting the lower water concentration, but are also more unsymmetrical, the center of the peak being shifted toward higher frequencies as SCN concentration increases. The upper limits (ca. 3620 cm^{-1} for OH and 2650 cm^{-1} for OD symmetric and asymmetric stretching modes, respectively) are for non-bonded water. This observation suggests that the apparent shift may be due to a decrease in the average hydrogen bonded cluster size influenced by the presence of succinonitrile.

3.3 Variable temperatures

FTIR-ATR spectrum of SCN-rich phase of the aqueous SCN system equilibrated at 21 °C cooled below this temperature exhibit a gradual shift in the nitrile stretching peak back to the position of pure SCN. Concomitantly there is a drastic change in the size and symmetry of the OH stretching band so that it resembles the OH stretching band of the SCN-rich phase.

Additionally, when a constant composition SCN-rich phase of the aqueous SCN system is equilibrated at 21°C, and warmed above its equilibration temperature, its FTIR-ATR spectrum shows a consistent decrease in the intensity of the lower "branch" of the OH band (Fig. 10). The large intensity decrease in the lower frequency branch is not compensated by intensity increases in the higher frequency branch. Hence, the effect is not simply a redistribution of water cluster sizes induced by higher equilibration temperature. Furthermore, there is some evidence that the intensity decrease is reversible. The final equilibration temperature (in Fig. 10) represents a very short equilibration time, about 30 minutes at 21°C. It is clear that equilibration results in an increase in the lower branch intensities over those at 53°C equilibration. To demonstrate reversibility would require at least a 24-hr equilibration. This would indicate a purely temperature dependent "reordering" of the solution. The observed temperature dependent OH stretching shift is similar to the OH shift seen during increasing SCN concentration at constant temperature. We believe that there is a decrease in the amount of water participating in the water-water hydrogen bonds at higher temperatures because of higher water fugacity and the presence of succinonitrile. Increased interaction with succinonitrile would explain the decrease in water accountability determined from the DSC data [6] at higher as compared to lower equilibration temperatures. Furthermore, a high concentration of SCN-water aggregates, not easily adsorbed on hydrophilic surfaces, could result in the adsorbed layer having a

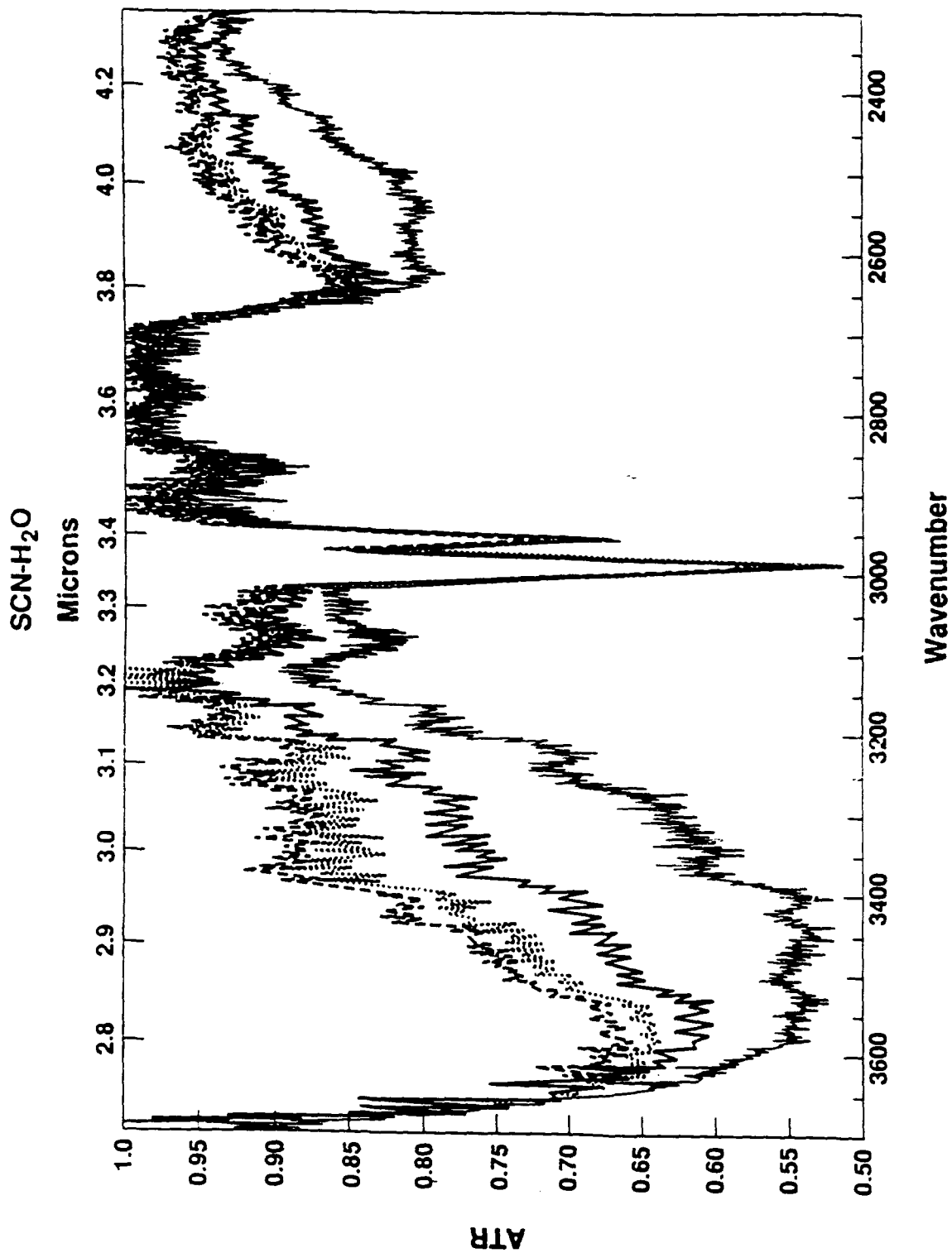


Fig. 10 Variation of OH symmetric (3200-3620 cm⁻¹) and OD asymmetric (2375-2650 cm⁻¹) stretching bands with temperature

Equilibration Temperature
 — 21°C (Initial)
 40°C
 - - - 53°C
 — 21°C (Final)

higher water concentration at higher temperatures.

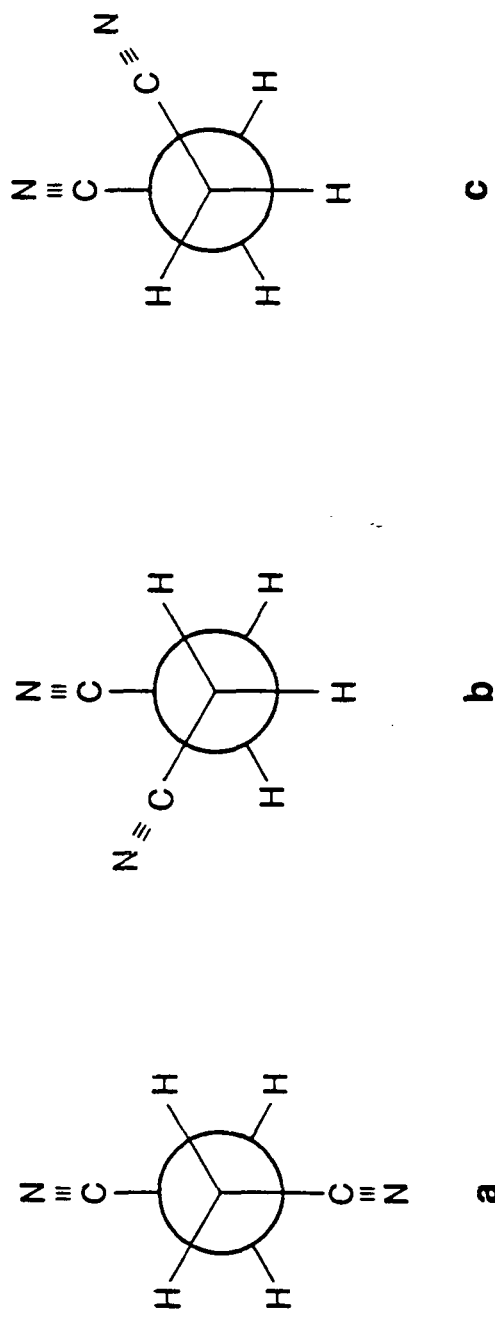
3.4 Raman spectroscopic experiments

Raman spectroscopy was used to determine the preferred bulk phase cluster profile in homogeneous succinonitrile-water solutions at different temperatures and compositions.

As a symmetrical 1,2-disubstituted ethane, the succinonitrile molecule is able to rotate freely about its principal axis, i.e., the central C-C single bond. This results in an equilibrium mixture of three stable rotational isomers, namely, the trans conformer (Fig. 11a) and two spectroscopically equivalent gauche conformers (Fig. 11, b & c). The two nitrile groups are 180° apart in the trans conformation (C_{2h} symmetry) and are 60° apart in the gauche conformations (C_2 symmetry).

It is generally agreed that both the trans and the gauche exist in the highly disordered liquid and solid states, with the two gauche conformations of lower energy by 360 cal/mole from the trans. When the solid is cooled to about 230 K, a totally ordered phase is formed, which consists only of the gauche conformations. Both conformers are found to co-exist in solutions. In strongly dipolar solvents, the gauche conformers are more stable than the trans conformer [9,10].

The vibrational assignments and normal coordinate analyses for the gauche and trans conformers have been made [9,11]. Although many of the IR and Raman bands for the gauche overlap with those for the trans conformer, there are some bands that are purely due to the excitations of either trans or gauche conformation (see Table 1). The presence of these bands is used



GAUCHE

TRANS

Fig. 11 The trans and gauche isomers of succinonitrile

Table 1 Raman frequencies (in cm^{-1}) for succinonitrile

Room Temperature ^a	230 K ^b	Gauche	Trans
357		C-C≡N bend	
388	385	C-C≡N bend	C-C≡N bend
478	490	C-C-C bend	
510			C-C-C bend
603	603	C-C-C bend	
812	813	CH ₂ rock	
951	975	C-CN stretch	C-CN stretch
1025	1033	C-C stretch	C-C stretch
1202	1200	CH ₂ twist	CH ₂ twist
1331	1328	CH ₂ wag	
1425	1430	CH ₂ bend	
2255	c	C≡N stretch	C≡N stretch

^aReference 11; ^bReference 10; ^cnot determined

as an indication of the existence of these rotational isomers. The 514-cm^{-1} band is due exclusively to the trans conformer, whereas the 954-cm^{-1} band is due exclusively to the gauche conformer. Therefore, at room temperature it can be seen that both gauche and trans conformers exist in pure solid SCN (Fig. 12a), or in 75% SCN/H₂O system (Fig. 13a), or in 15% SCN/H₂O system (Fig. 14a). However, at -50°C , Only gauche conformer exists in pure SCN (Fig. 12b) and in 75% SCN/H₂O system. But in the water-rich system (15% SCN/H₂O), it appears that both trans and gauche conformers still coexist.

4. DISCUSSION

FTIR-ATR and Raman spectroscopic analysis shows significant concentration dependency. Unfortunately, FTIR-ATR could not yield surface spectra since the evanescent infrared wave penetration depth into the bulk phase was far too great. All spectra, therefore, must be considered bulk-phase. The results of calorimetric experiments [6] have suggested that, in homogeneous SCN-water solutions, the water-rich clusters contain less associated SCN at higher temperatures than at lower temperatures. Furthermore, there are fewer water-rich clusters at higher temperatures, and hence a smaller quantity of water residing in such clusters. These observations were explained [6] on the basis of water fugacity and the variation of water-water hydrogen bonding in normal liquid water cluster distributions with temperature. It may be assumed that miscibility-gap type solutions, such as SCN-water, contain both "flickering" water-rich and SCN-rich clusters. In the presence of SCN, the chemical

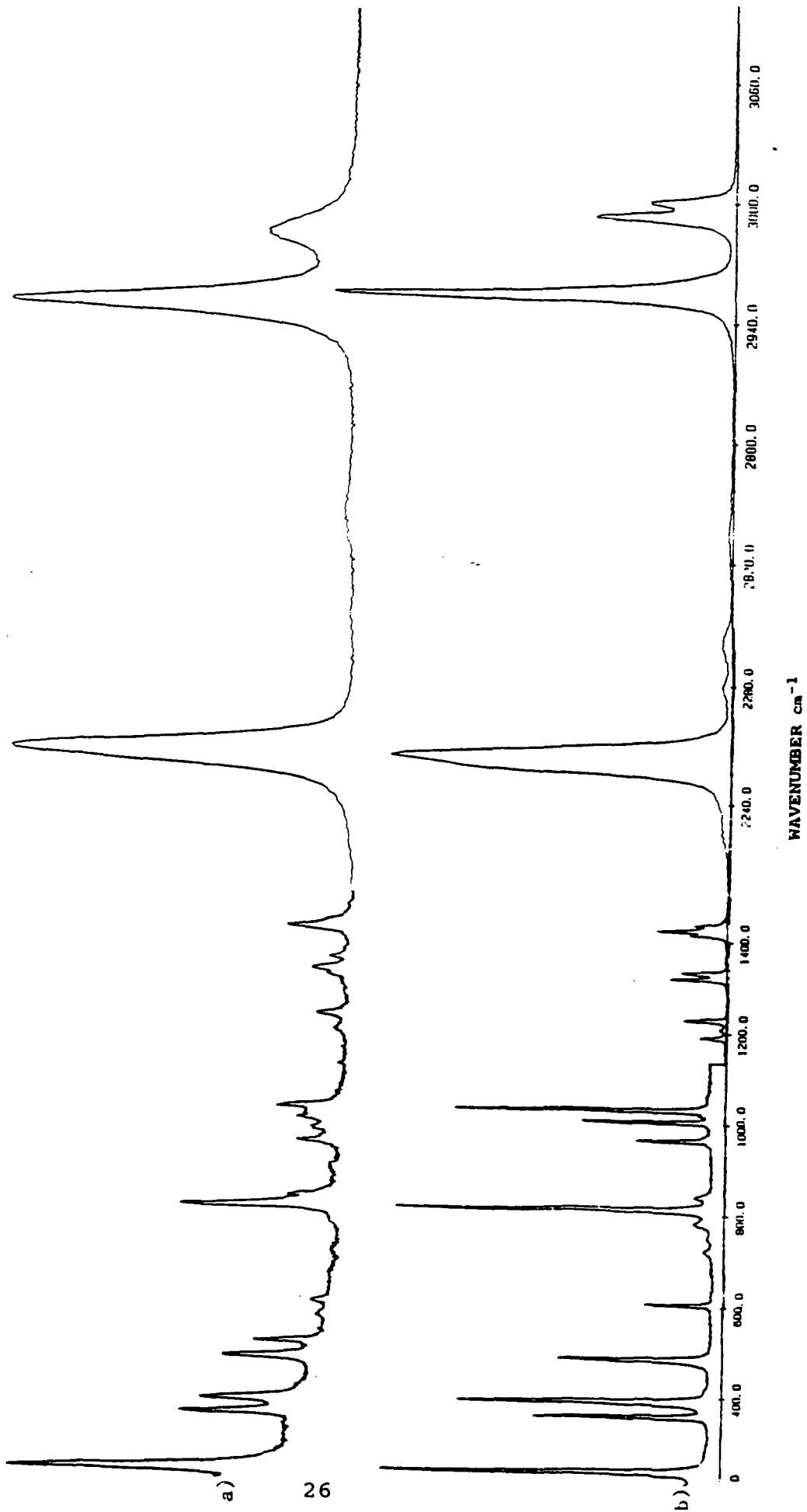


Fig. 12 The Raman spectra of solid succinonitrile
(a) at room temperature; (b) at -50°C

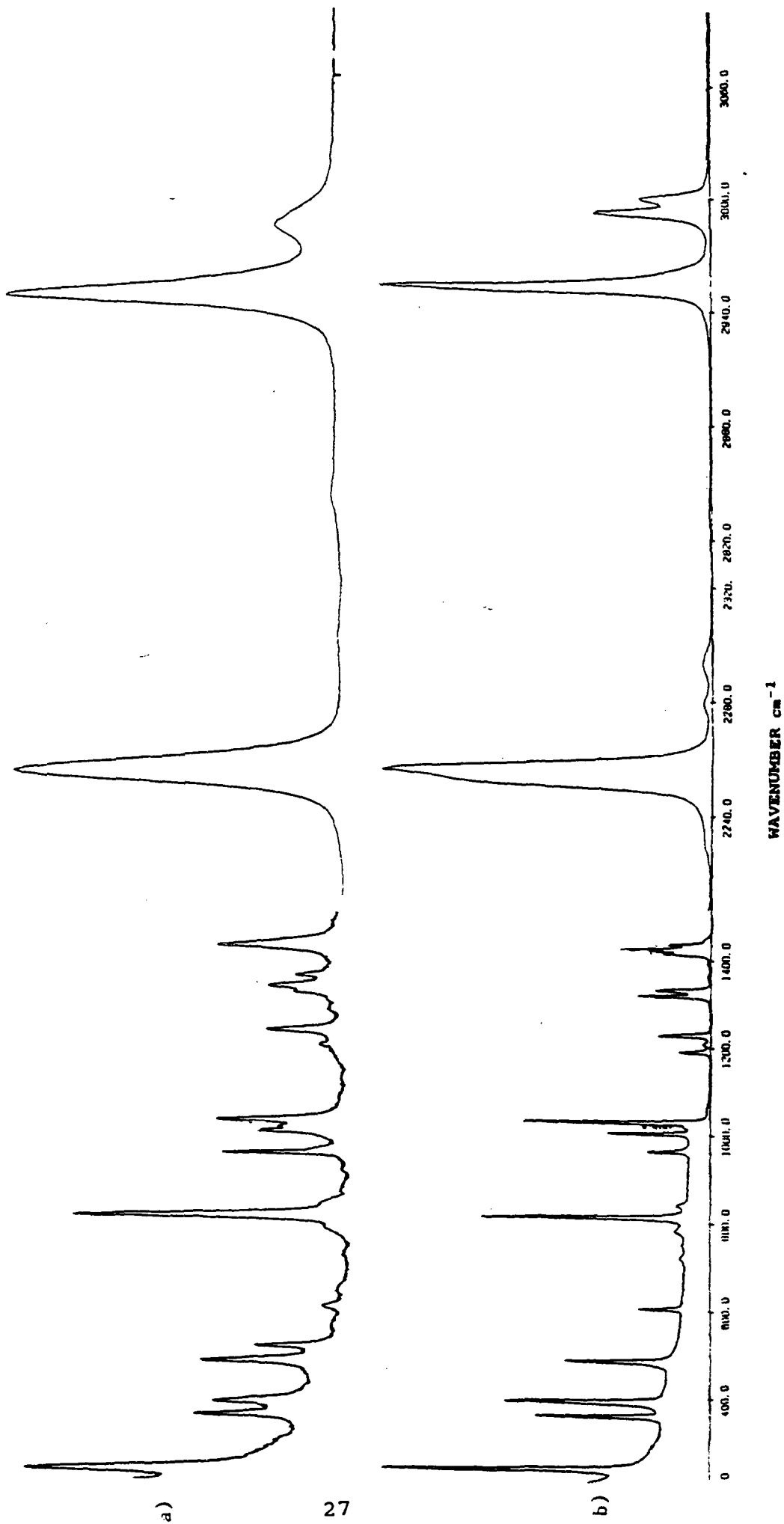


Fig. 13 The Raman spectra of 75% SCN/H₂O system
(a) at room temperature; (b) at -50 °C

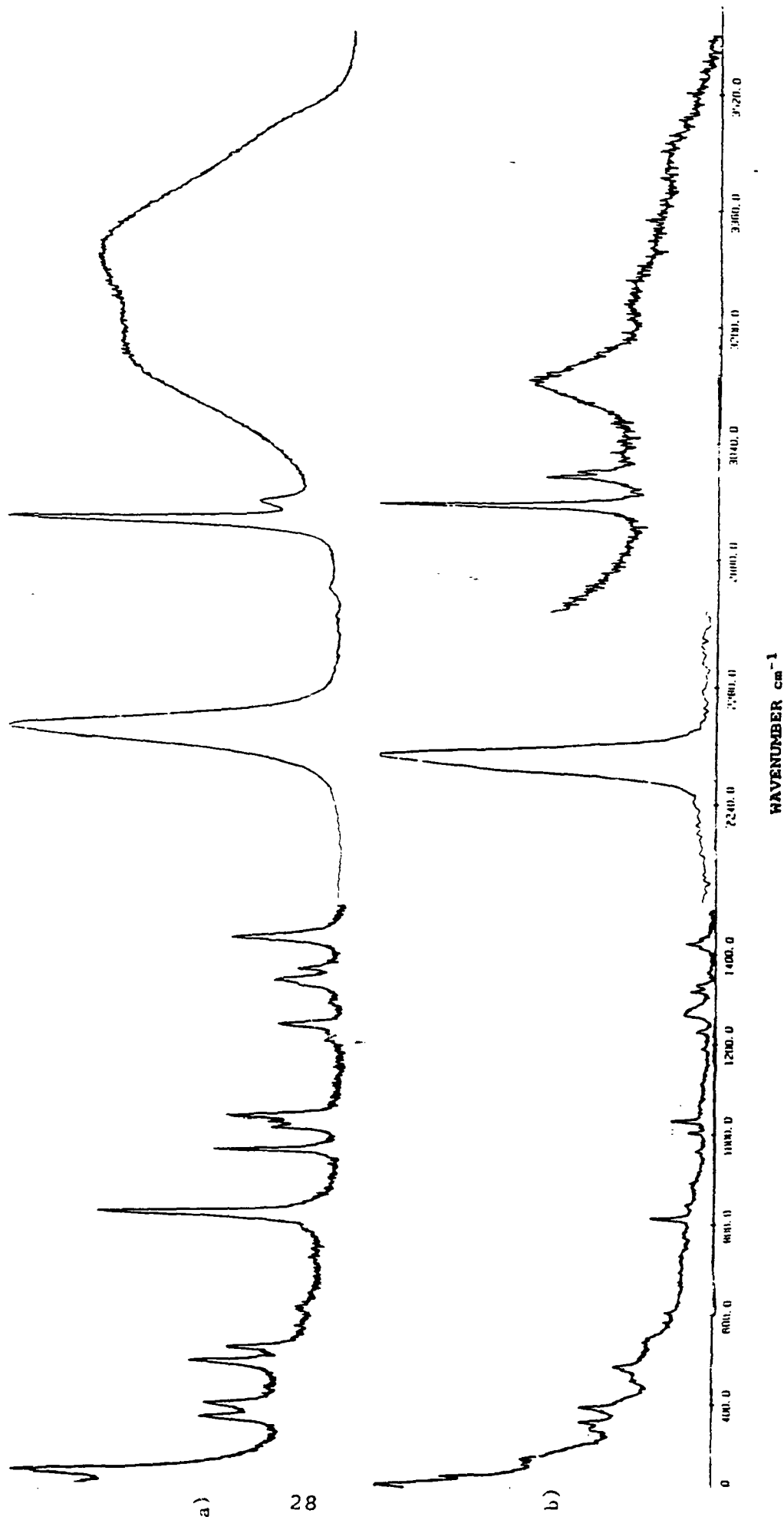


Fig. 14 The Raman spectra of 15% SCN/H₂O system
(a) at room temperature; (b) at -50 °C

potential of water demands that water be distributed between the SCN-rich and the water-rich clusters. At higher temperatures, a significant fraction of "escaping" water is non-bonded gaseous-type molecules in the liquid phase. Hence, the water-rich cluster contains less water than at lower temperatures.

Since there is a higher degree of water-water hydrogen bonding (i.e. less non-bonded water) at lower temperatures, it is assumed that SCN-rich and water-rich clusters associate for homogeneity (in a single phase solution). Hence, at higher temperatures, water-rich clusters must be more highly associated with SCN than water-rich clusters. This seems reasonable if we consider that "escaping" water exists as hydrogen bonded clusters which can transform formerly SCN-rich clusters into water-rich clusters, which still contain relatively high concentrations of SCN. There is more non-bonded water present at higher temperatures because of the higher water fugacity at higher temperatures.

Generally, larger quantities of SCN interact with non-bonded water at higher temperatures causing a low degree of undercooling upon monotectic solidification, and low water accountability in the DSC freeze/melt data [6], since non-bonded water is incapable of freezing. At lower temperatures, large quantities of SCN are associated with water hydrogen-bonded clusters which results in depletion of SCN in the solidifying bulk at the monotectic temperature, and an apparently much higher degree of undercooling.

The broad OH stretching band of pure water is shifted to

lower frequencies as SCN-water interactions increase. Also, the OH band broadens with decreasing temperature. This suggests that the degree of water-SCN association increases as the temperature decreases. The water-rich clusters are fully associated with succinonitrile, and no non-bonded water remains in the water-rich distribution at phase separation. Concomitantly, from about 55 °C the OH (or OD) stretching band shows a significant increase upon lowering the temperature.

These trends are consistent with a reduction in water-rich clusters at the higher temperatures, and with the increase in the quantity of the water-rich "phase" and greater SCN-water association as temperatures approach the miscibility gap. Upon crossing into the two phase region, the OH stretching band decreases dramatically, as does the frequency shift toward 3300 cm^{-1} . The HOH (and DOH) bending band is relatively insensitive to temperature changes in the homogeneous region and only the intensity increases notably (indicating an increase in water concentration near the ATR cell) in the two phase region. Changes in both the OH stretching and HOH bending bands are reversible as temperature is allowed to fluctuate up and down. These observations are consistent with the calorimetric results [6].

Although the CN stretching peak in the SCN phase showed no noticeable shift in frequency with a change in temperature, the SCN peak increased significantly with decreasing SCN concentration in the homogeneous region of the phase diagram ($T > 55\text{ °C}$). This shift is consistent with head to head hydrogen bonding between the CN nitrogen and the water hydrogen. All SCN peaks showed changes in intensity reflecting changes in relative

SCN-water concentrations.

The OH stretching and HOH bending bands in pure water show very little shift in frequency or change intensity as a function of temperature, it seems therefore that the variations observed in the SCN solutions are due to presence of SCN and in the interpretation presented herein to the temperature dependent cluster distributions.

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