

Spectra and structure of binary azeotropes V-acetone–cyclopentane

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Abstract

Acetone and cyclopentane make a minimum boiling homogeneous binary azeotrope with mole ratio 2:3. Some characteristic vibrational modes, as well as ^1H NMR signals change due to the azeotrope formation. The extend of interaction of these molecules causes significant changes on some vibrational modes involved and ^1H NMR signals show some changes on their position. In this work the FTIR and ^1H NMR spectra of pure acetone, pure cyclopentane and corresponding azeotrope were recorded, mutual influences resulting from azeotrope formation have been analyzed, and spectral changes has been discussed. The unit-structure of cluster have been deduced, based on mole ratio, boiling point depression of constituents, and comparison between the spectra obtained by FTIR and ^1H NMR techniques.

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1. Introduction

Among the many searching exploratory investigations of H-bonding, the magnitude and sign of the shifts in frequencies of vibrational modes closely associated with hydrogen bond formation have long served as important diagnostics of the presence and strength of H-bonding [1–8]. Also, it has been shown that NMR techniques have been very fertile applied to the study of hydrogen-bonded systems in solution [9–17]. This success is due to the large chemical shifts experienced by proton when they become involved in hydrogen bonds and to the accuracy with which these shifts may be measured.

Acetone and cyclopentane make a binary azeotrope with maximum vapor pressure, which its unit-structure is completely unknown. There have been some spectroscopic investigations of acetone–cyclopentane mixtures [18–24], but there has not been any specific attempt to determine unit-structure of their azeotrope and/or corresponding IR and NMR spectra. Azeotrope's unknown structure was a good motive for us to determine its structure by investigating FTIR and ^1H NMR spectra of constituents and azeotrope which provides a lot of information on intermolecular forces and molecular orientation of components in the azeotrope.

2. Experimental

The chemicals acetone and cyclopentane were purchased from Merk. Acetone 99.9% with less than 0.1% water and cyclopentane were distilled for further purification and measuring their boiling points at laboratory pressure (733 mmHg). The binary azeotrope were prepared by adding appropriate quantities of the liquids by volume using micropipettes, mixture were fractionally distilled and a center fraction boiling at 37 °C was chosen from the same multiplate column. The mid-infrared spectra of pure acetone, pure cyclopentane and azeotrope was recorded on a Nicolet model 800 Fourier transform interferometer equipped with a high intensity Globar source, Ge/KBr beam splitter and DTGS detector. A resolution of 0.09 cm^{-1} was utilized and 400 interferograms were taken of both the sample and empty reference cell. The ^1H NMR spectra of acetone, cyclopentane and their azeotrope were obtained on a Bruker 500 MHz Model FT-NMR.

3. Results and discussion

Acetone and cyclopentane form a homogenous binary azeotrope with minimum boiling point in which the mole ratio of acetone to cyclopentane is 2:3. Pure samples of acetone and cyclopentane boil at 51.5 and 45.5 °C (at 733 mmHg), respectively, while their azeotrope boils at 37 °C. The 14.5 °C decrease in boiling point of acetone and 8.5 °C decrease in boiling point of

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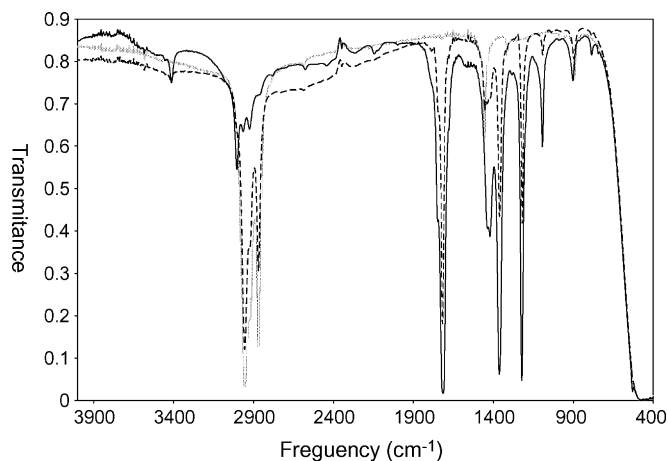


Fig. 1. FTIR spectra of acetone (—), cyclopentane (·····) as well as their azeotrope (---) at room temperature in the region 600–4000 cm^{-1} .

cyclopentane shows that due to the azeotrope formation, attraction forces between carbonyl moiety of one acetone molecule and its neighboring molecule in pure acetone has been diminished. Boiling point depression of acetone is significantly more than that of cyclopentane, this difference indicates that acetone molecules must be noticeably much more separated from each other, by losing their original dipole–dipole attraction, in the azeotrope.

Fig. 1 shows that C=O stretching mode in acetone has been shifted from 1714.4 to 1718.3 cm^{-1} in azeotrope (Table 1). This blue shift in C=O stretching mode indicates that strong attraction due to the dipole–dipole between adjacent acetone molecules [25] has been removed upon azeotrope formation. In pure acetone due to the tendency of hydrogen atoms for unpaired electrons on the neighboring oxygen atom, they are bounded to the oxygen atom, therefore in compare with an individual molecule; angle related vibrations of methyl groups need a little more energy to vibrate. Now if we separate acetone molecules (by vaporization, solvation or mixing with appropriate molecules) C=O bond will be a little shortened and hydrogens in methyl group will be unbounded, consequently C=O and C–H stretching modes need more energy to vibrate (blue shift). While C=O

and CH₃ stretching modes show blue shift, we expect red shift for CCO bend and CH₃ deformation. As Davies pointed out [26], it would be anticipated that the potential field governing all the vibrations of the carbonyl and methyl groups will be influenced simultaneously. Thus while acetone molecules are separated, their C=O and C–H bonds become shorter causing an increase in their stretching frequency, therefore in comparison with pure state, it will tend to tie in the hydrogens more loosely in their angular orientation. Consequently, the deformation frequencies can be expected shift to lower frequencies upon dissociation (red shift).

Observed spectrum (Fig. 1) exactly verifies above discussion. As it can be seen from Table 1, CH₃ symmetric deformation (1363.4 cm^{-1}), CCO bending (1222.7 cm^{-1}) and asymmetric rock (1093.4 cm^{-1}) are shifted to lower frequencies (1361.5, 1220.7 and 1091.5 cm^{-1} , respectively).

Considering the mole ratio of acetone to cyclopentane in their azeotrope (2:3), we predict that cyclopentane molecules be relatively less isolated. The 8.5 °C decrease in boiling point of cyclopentane indicates that these molecules are isolated from each other, which causes decrease in bulk attraction forces. Clearly, going from a condense phase to vapor phase, diluting a liquid, or mixing sample in a suitable matrix, can cause an increase in the frequency of the vibrational mode. Hence, cyclopentane molecules get separated from each other by acetone molecules, therefore, C–H stretching modes are expected shift to the higher frequencies due to the decrease in the intermolecular attraction forces. Fig. 1 shows that this has been actually happened. The blue shift of C–H stretching mode of methylene groups ($\Delta\nu = 1.9 \text{ cm}^{-1}$) verifies above prediction. Here, we may consider another reason for this blue shift: it is well understood that cyclopentane actually assumes a slightly puckered “envelope” conformation that reduces the eclipsing and lowers the torsional strain. This puckered shape is not fixed in one conformation but undulates around the ring by the thermal up-and-down motion of the five methylene groups. The “flap” of the envelope seems to move around the ring as the molecule undulates. Compared with the corresponding straight-chain alkenes, the cycloalkanes have higher boiling and melting points, as well as higher densities. This is due in large part to increased London interactions of the relatively more rigid and more symmetric cyclic systems. Therefore, it is predictable that cyclopentane molecules loose a lot of London attraction forces upon solvation or mixing with other molecules, which in turn shortens C–H bond length and consequently we see blue shift in the vibrational spectrum. The 1.9 cm^{-1} blue shift in C–H stretching modes of CH₂ groups in azeotrope (Table 1) indicates that cyclopentane molecules not only must be separated from each other, but, methylene moieties must be held by carbonyl groups on acetone, which makes undulation more difficult than before. The result of this phenomenon is that the bending modes of CH₂ groups must also be constrained. As result of this limitation, the vibration needs more energy, which means blue shift for CH₂ bending modes in the azeotrope. The observed frequency (Fig. 1) and Table 1 show an increase in frequency of CH₂ bending modes in the azeotrope ($\Delta\nu = 1.9 \text{ cm}^{-1}$) which confirms above anticipation.

Table 1

Vibrational frequencies of acetone, cyclopentane and acetone–cyclopentane azeotrope, along with frequency shifts in azeotrope with respect to corresponding bands in pure substances^a

| Vibrational mode | ν (cm^{-1}) acetone | ν (cm^{-1}) cyclopentane | ν (cm^{-1}) azeotrope | ν (cm^{-1}) |
|-------------------------|---------------------------------------|--|---|----------------------------|
| CH ₃ a. str | 3004.6 | – | 3006.4 | 1.9 |
| C=O str | 1714.4 | – | 1718.3 | 3.9 |
| CH ₃ s. def | 1363.4 | – | 1361.5 | –1.9 |
| CCO bend. | 1222.7 | – | 1220.7 | –2 |
| CH ₃ a. rock | 1093.4 | – | 1091.5 | –1.9 |
| CH ₂ a. str | – | 2952.5 | 2954.4 | 1.9 |
| CH ₂ a. def | – | 1454.1 | 1456 | 1.9 |
| CH ₂ rock | – | 892.9 | 894.8 | 1.9 |

^a Only those frequencies which have been observed and/or have measurable frequency shift are listed.

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