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# Structure of hexafluoroisopropanol–water mixture studied by FTIR-ATR spectra and selected chemometric methods

Bogusława Czarnik-Matusewicz [a,*], Sylwia Pilorz [a], Li-Ping Zhang [b], Yuqing Wu [b]

[a] *Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland*
[b] *State Key Laboratory for Supramolecular Structure and Materials, Jilin University, No. 2699 Qianjin Street, Changchun 130012, PR China*

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## Abstract

The FTIR spectra of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)–water binary solutions have been obtained by means of attenuated total internal reflection (ATR) spectroscopy. The spectral properties of the system have been analyzed as a function of alcohol concentration by following methods: multivariate curve resolution based on alternating least-square procedure (MCR-ALS) preceded by evolving factor analysis (EFA), kernel analysis, and two-dimensional (2D) correlation spectroscopy. From all the information obtained by these methods the four-component model describing the aggregation of HFIP and water molecules in HFIP–water mixtures was proposed. In characterization of properties of the components not only changes in the aggregation process were taken into account but also variations in relative population of different HFIP conformations were considered. The case reported is a very good example to show how the MCR-ALS and 2D analysis could complement each other, leading to enhancement of the multicomponent data interpretation.

*Keywords:* 1,1,1,3,3,3-Hexafluoro-2-propanol; HFIP; Multivariate curve resolution; MCR-ALS; Two-dimensional correlation spectroscopy; 2DCOS

## 1. Introduction

Among various fluoro-alcohols 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) is the most effective in stabilizing the α-helical structure of peptides and proteins [1]. For better understanding of HFIP's role in the process an advanced studies under the detailed structure of its aqueous mixture were undertaken [2]. Available results demonstrate that HFIP clusters formed in HFIP–water binary solution are essential for understanding the physicochemical properties of aqueous HFIP mixtures and their role in controlled denaturation of the native structures of proteins [3,4]. Most frequently both theoretical and experimental studies of the HFIP–water systems are focused on describing properties of the system around 30% HFIP volume.

In present paper, we have performed ATR-FTIR measurements for the HFIP–water mixture over a whole range of HFIP mole fraction to describe the structural properties of HFIP–water binary solutions as a function of alcohol concentration. Such procedures as evolving factor analysis (EFA), principal components analysis (PCA), multivariate curve resolution-alternating least-squares (MCR-ALS), kernel analysis, and generalized two-dimensional correlation spectroscopy (2DCOS) have been employed to analyze the FTIR-ATR spectra. Obtained results confirm known facts about HFIP–water structure in a water-rich region and enhance the incomplete knowledge about aggregation of HFIP in a water-poor region.

## 2. Experimental procedures

HFIP of the best available purity grade was purchased from ABCR GmbH & Co. KG (Germany). The water used for preparing of the solutions first was double distilled and

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[*] Corresponding author.
*E-mail address:* bc@wchuwr.pl (B. Czarnik-Matusewicz).

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next followed by deionization using a Simplicity 185 Water System (Millipore). The HFIP–water mixtures over a wide range of volume concentration of HFIP, i.e., from 0% to 100% with a step of 5% were prepared by weighing of appropriate amounts of alcohol and water at temperature of 25 °C.

ATR-FTIR spectra were collected on a Nicolet Magna FTIR 860 spectrometer equipped with Globar source, KBr beam splitter and DTGS detector. An ATR cell incorporating 45° Ge crystal with 10 internal reflections supported into cartridge heater for heating the crystal plate (Pike Technologies) was used for the measurements carried out at 25 °C, at resolution of 1 $cm^{-1}$. The temperature was monitored by Watlow 988 controller with accuracy of ±0.2 °C (Watlow, Missouri, USA).

Prior to the multivariate analysis, the data were subjected to some carefully selected pre-processing steps. The first one involved ATR correction aimed on estimating a depth of penetration of the evanescent wave (i.e., the optical path length). The main subject of our interest in this paper was to investigate a relation between the concentration changes and structural properties of the HFIP–water system that can be directly resolved from spectral variations only a range below 1500 $cm^{-1}$, which has been examined in detail. To make the subtraction of water absorbance quantitatively as much as possible the procedure proposed by Dousseau et al. was used [5]. In a next step the subtracted spectra were subjected to a baseline correction in analyzed range using a linear function. Final step concerned a minimization of common absorbance changes arising from concentration increase leading the same increment of absorbance at each wavenumber that is out of our interest. An extent of the common changes is much larger than the uncommon ones arising from variations of the intra- and intermolecular aggregation of the HFIP–water molecules accompanying the concentration increase of HFIP. It is necessary to reduce the major linear variations as it amplifies the nonlinear minor changes that carry out the information about processes developed in the system. The integral absorbance values calculated for each spectrum in the 1500–780 $cm^{-1}$ range were used as a normalization factor. Fig. 1 presents the finally obtained spectra that have been subjected to further analysis.

All the steps were carried out by the GRAMS/32 AI ver. 6.00 program package (Galactic Industries Corporation), RAZOR program (Spectrum Square Associates, Inc. Ithaca, NY) also running under the GRAMS software and by our custom written MATLAB scripts (The Math Works, Inc.).

The finally preprocessed spectra have been arranged into data matrix (**A**), with *m* rows and *n* columns, with each variable (wavenumber) being a column and each sample (spectrum for given concentration) a row. The matrix **A** has been transferred into the Matlab computational environment because the calculations of kernel, as well as synchronous and asynchronous matrices were done by our custom written Matlab scripts. Also the EFA calculations and MCR-ALS analysis were performed in Matlab using the freely available program from Tauler's group [6].

## 3. Results and discussion

### 3.1. Multivariate curve resolution-alternating least squares

In MCR-ALS analysis the spectral data combined in matrix **A** are decomposed according to the simple bilinear model into two matrices **T** and **P** according to the following linear model:

$$\mathbf{A} = \mathbf{T}\mathbf{P}^{\mathrm{T}} + \mathbf{E}. \quad (1)$$

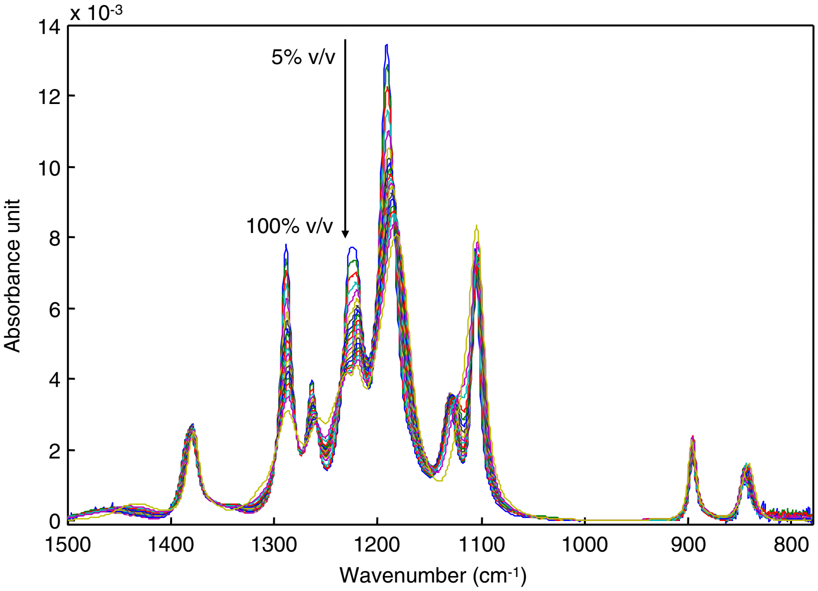

Fig. 1. Finally preprocessed FTIR-ATR spectra of HFIP–water mixtures in a range 1500–750 $cm^{-1}$ presented in function of varying concentration of HFIP from 5% to 100 % (v/v). Trend of the spectral changes with increasing concentration of HFIP is indicated by an arrow.