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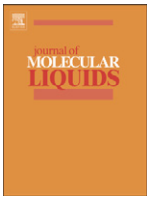

Infrared spectroscopy of liquid water–*N*,*N*-dimethylformamide mixtures

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ABSTRACT

The real and imaginary molar polarisability spectra ($\alpha'_m(\tilde{\nu})$ and $\alpha''_m(\tilde{\nu})$, respectively) of mixtures of water and *N*,*N*-dimethylformamide (DMF) over the full composition range ($0 \le x_{DMF} \le 1$) at 25 °C were determined between 4000 and 700 cm^{-1} by using a calibrated single reflection attenuated total reflection (ATR) technique. The composition dependent mole fractions of OH groups hydrogen bonded to water or DMF, together with the fractions of carbonyl groups hydrogen bonded to water or free were obtained from the integral intensities C_{OH}, and C_{CO} of the ν(OH) and ν(CO) bands, respectively. As for the acetonitrile-water system (studied by other groups), a continuous composition dependence of the mole fraction of OH oscillators in different bonding situations was found with practically the same segmentation of the full composition range ($x_I = 0.2$–0.3, $x_{II} = 0.7$–0.8). From these observations, the existence of relatively large, stable water or DMF aggregates is proposed for x_{DMF} between x_I and x_{II} with hydrogen bonding between water and DMF occuring only at the interfaces between the aggregates.

1. Introduction

Formamide (F), *N*-methylformamide (MF), *N*,*N*-dimethylformamide (DMF), acetamide (A), *N*-methylacetamide (MA) and *N*,*N*-dimethylacetamide (DMA) are the simplest amides. Some of them are important as organic solvents and/or as model systems for peptides (in particular MA). Their interaction with water is paramount to understanding the role of water in the behaviour of peptides in biological media. They represent two significantly different classes of solvents. For example, F and MF, having hydrogen atoms bonded to nitrogen, have both hydrogen-bond donating and hydrogen-bond accepting abilities. On the other hand, DMF and DMA contain only a hydrogen-bond accepting carbonyl group. Amide molecules have large dipole moments (3.36 D for F, 3.87 D for MF, and 3.82 D for DMF [1]) and dipole–dipole interactions are also expected to play an important role in determining liquid structure. At shorter distances molecules cannot be approximated with point multipoles and short-range ordering which is claimed to exist in pure polar liquid certainly cannot simply be accounted for by (anti)parallel orientation of two dipoles. Besides specific (hydrogen bonding) and non-specific (multipole–multipole) interactions, intermolecular repulsion (in the first approximation best expressed through the differences in molecular shapes and volumes) at very short distances must also be taken into account. Aqueous amide systems are only a part of much greater group of aqueous mixtures of non-electrolytes that have been studied in details over the years. Their thermodynamic functions have been measured on numerous occasions [2–5]. Partially as a result of hydrogen bonding, preferential solvation (when the local mole fraction of water in a solvation microsphere surrounding a solvate molecule differs from the bulk one [6]) occurs in aqueous amide systems. It was possible through the comparative analysis of large number of such systems to reveal their general characteristics long ago [7]. These are (i) negative signs of enthalpy and entropy of mixing for the very low concentrations (less than $x = 0.1$) of the organic component, and (ii) negative values for the partial molar enthalpy and entropy of water for medium concentrations. The structure of such a mixture depends on its composition and it was possible to empirically establish the composition ranges within which the structure can be considered more or less preserved. In other words, for a given binary system any of its excess properties should be explainable in terms of always the same number of sub-intervals in the composition range. This number for amide–water mixtures is four and the composition values defining the sub-intervals are $x_I = 0.075$, $x_{II} = 0.25$ and $x_{III} = 0.50$, with the microheterogenous range being between x_{II} and x_{III} [8].

Amide–water mixtures have been also extensively studied by molecular dynamics simulations. In such an approach the structure of the liquid is understood as all that comes out from the analysis of pair radial distribution functions, $g(r)$[X–Y], giving a measure of the probability of finding an atom Y at the distance r from an atom X (actually, $\rho g(r)dr$ is that "probability", not normalized to unity, but to the number of particles N, and thus, $\rho(r) = \rho g(r)$ is a local density about some fixed molecule). It is generally assumed that from the positions of maxima of the pair radial distribution functions the structure of the first and even more distant solvation shells can be derived. From the two distinct peaks near 2.7 and 6.4 Å of $g(r)[O_{DMF}–H_{DMF}]$ [9], for example, an indication for the weak hydrogen bonding has been

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evoked. Since the interatomic distance is not the only criterion for the existence of hydrogen bonding, the other being the C–H···O angle, the number of times the formyl hydrogen is taking part in hydrogen bonding can only be counted for a given snapshot. In such a way it has been found that only around 30% of either formyl or methyl hydrogens in pure DMF are engaged in hydrogen bonding situations. The increase in the peak intensities of $g(r)[\mathrm{O_W{-}H_W}]$ with x_{DMF} is intepreted as the tendency of water to stay in aggregates. Even more, since non-electrolytes are generally claimed to enhance the structure of water in very diluted solutions [7], the intensity increase of $g(r)[\mathrm{O_W{-}H_W}]$ was identified with such a property of DMF. Much more relevant data for the results we are going to present below are the plots showing the fractions of water or DMF oxygen atoms engaged in a particular type of hydrogen bonding. The average number of hydrogen bonds/water molecule in pure water is 3.3 and not 4, as is required for fully tetrahedral water.

Recently, yet another molecular dynamics simulation study of neat and aqueous amides have been conducted in order to investigate both the cluster distribution and pair structure factors [10]. The fact that no specific cluster formation has been seen either for water or any of the neat amides need not be in contrast to the generally accepted understanding of them as more or less structured liquids due to their ability to form hydrogen bonds. The anaylsis of clustering has not been performed for mixtures, although they have been described in a different way. They are all strongly microheterogenous at the nanometer/nanosecond scales [11] and therefore a possible way to observe that in IR spectra would be to calculate the excess spectra and see the size of the deviations from the ideal behaviour. Saying it differently, if there exist microheterogeneities of that size the spectrum of a mixture should nearly look as a weighted sum of the pure liquid spectra.

Water and DMF are neat liquids and their mixtures have also been extensively studied by vibrational spectroscopies because for investigation of hydrogen bonding, generally and particularly in liquid water and binary aqueous mixtures, one of the most sensitive methods is infrared spectroscopy [12]. Neat liquids are at the limits of the full composition range and their spectra are to be considered as (unperturbed) reference spectra. The mid-IR spectra of pure water and pure DMF are well known, although the interpretation of the former is far from being settled down. In a recently published paper, Stangret *et al*. report on the details of the hydration sphere of simple amides extracted from the solute affected water spectrum obtained in the limit of infinite dilution [13]. The analysis is also based on the hypothesis that the position of the OD stretching band of HDO isotopically diluted in H_2O can be correlated with interatomic O–O distances [14]. There should be around 30 water molecules in the first hydration sphere of a DMF molecule and only two to three of them affected by the interaction with the amide molecule.

The possibility of CH···O hydrogen bond interactions in pure DMF has also been studied by infrared spectroscopy [15]. Although the hydrogen bonding between formyl hydrogen and carbonyl oxygen in solid DMF is present, it seems to be too weak to exist for longer times in the liquid DMF. The upshift of the ν(CH) bands of DMF with increasing water content was observed and it was also noticed that the carbonyl band in pure (no cosolvent) aqueous (D_2O) solutions was a single symmetrical feature as if all the carbonyl groups were hydrogen-bonded to water [16]. In the Raman study of the ν(OH) of this system [17] the changes in the 3800–3100 $\mathrm{cm^{-1}}$ region were interpreted in terms of the weakening of hydrogen bond network (the local tetrahedral structures of liquid water are strongly deformed with increasing the fraction of DMF).

Considerable progress in quantitative infrared spectroscopy of aqueous mixtures has been achieved by use of attenuated total reflection (ATR) to measure accurately intensity quantities [18]. The existing procedure for calculation of infrared optical constants from ATR($\tilde{\nu}$) spectra, namely index of refraction, $n(\tilde{\nu})$, and absorption index, $k(\tilde{\nu})$, by modified Kramers-Krönig transform allows very accurate determination of infrared band intensities [19]. The optical constants of water have been measured and are now available as a secondary intensity standard [20].

To our knowledge, there is no infrared study in which the optical constants of pure and aqueous DMF have been measured. Therefore, IR spectra of water–DMF mixtures over the whole composition range ($0 \le x_{\mathrm{DMF}} \le 1$) were measured using ATR technique in order to complement with new details the already existing picture of the structure of aqueous amides. The measurement of the composition dependent integral intensities of the bands in the wavenumber weighted imaginary molar polarisability spectra, $\tilde{\nu}\alpha''(\tilde{\nu})$, allows determination of mole fractions of OH oscillators involved in hydrogen bonding and in other bonding situations. The underlying assumption is that of partitioning of the integral intensity of the ν(OH) and ν(C═O) bands into two constant terms weighted by the mole fractions. Together with the results of molecular dynamics simulations [9,10], and measurements of their thermodynamic properties [2–5], this is the basis for further discussion of the structure of liquid water–DMF mixtures. We will compare our data with those obtained for a similar system of acetonitrile–water mixtures by the same method [21], or by the factor analysis [22], or by the spectral deconvolution [23].

2. Experimental

For the sample preparation, triple distilled water was used. Anhydrous DMF from Aldrich was used without further purification. The mixtures for all measurements were prepared gravimetrically, with a precision in mass of $\pm 10^{-5}$ g, and in mole fractions of $\pm 10^{-4}$. A series of samples, ranging from pure water to pure DMF, was prepared.

The spectra were obtained with an ABB Bomem MB102 Fourier-transform infrared spectrometer with a DTGS detector and CsI optics. Specac's Golden Gate single-reflection ATR system with diamond as internal reflection element and beam condensing optics made of ZnSe was used. The angle of incidence was 45°. Each ATR($\tilde{\nu}$) spectrum was recorded as the ratio of the ATR element covered by the sample to the spectrum of the dry ATR plate, that was recorded before measuring each sample. Each spectrum represents an average of 100 Fourier-transformed interferograms. The nominal resolution was 2 $\mathrm{cm^{-1}}$, which means that the distance between points in the resulting spectra is $\Delta\tilde{\nu} = 1\ \mathrm{cm^{-1}}$. All measurements were taken three times and averaged to give the final values for each mixture. The standard optical constants of benzene [24] and water [20] were used to determine effective number of reflections, which was found to be $m = (0.74 \pm 0.03)$. All the spectra were recorded at (25 ± 2) °C.

Refraction indices were measured with an Abbe refractometer PZO Warszava RL3, using low-pressure sodium lamp ($\lambda = 589.29$ nm). Precision of the refraction indices was determined by measuring refraction indices of water (25 °C) and *N,N*-dimethylformamide (20 °C), and comparing them with literature data [25]. Estimated precision in refraction index is ±0.0001, while the temperature of the cell was stable within ±0.2 °C.

Densities were measured by vibrating-tube densitometer Mettler-Toledo DE50. Precision of the density measurements, which is $\pm 1.2 \cdot 10^{-6}\ \mathrm{g\ cm^{-3}}$ was determined by measuring the density of triple redistilled water at 25 °C, and comparing it with literature data [25]. The temperature in the U-tube of the densitometer was stable within ±0.1 °C.

2.1. Data treatment

The negative decadic logarithm of an ATR($\tilde{\nu}$) spectrum defines the *p*ATR($\tilde{\nu}$) spectrum. From these spectra, optical constant spectra, $n(\tilde{\nu})$ (refraction index) and $k(\tilde{\nu})$ (absorption index), were obtained for the 4000–700 $\mathrm{cm^{-1}}$ region by using the program PKREF (Version 05/2000) [19]. This procedure requires refraction index at wavelength far