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Infrared optical constants, molar absorption coefficients, dielectric constants, molar polarisabilities, transition moments and dipole moment derivatives of liquid *N*,*N*-dimethylacetamide–carbon tetrachloride mixtures

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ABSTRACT

Mid-infrared spectra of the DMA–carbon tetrachloride system by transmission and single- and multiple-reflection ATR technique in the whole composition range ($0 < x_{\mathrm{DMA}} \leq 1$), recorded at room temperature between 5000 and 850 cm^{-1} are presented. The complex optical constant, molar absorption coefficient, complex dielectric constant and complex molar polarisability spectra are determined. The wavenumber × imaginary molar polarisability spectra were fitted to classical damped oscillator model, which gives intensities, vibrational transition moments, and dipole moment derivatives with respect to normal coordinates of the corresponding vibrations.

1. Introduction

It is expected that simple amides without hydrogen atoms directly bonded to nitrogen have no possibility of hydrogen bonding strong enough to exist in liquid state. The simplest representatives of such molecules are *N*,*N*-dimethylformamide (DMF) and *N*,*N*-dimethylacetamide (DMA). Here represented is the first part in a series of papers dealing with intermolecular interactions of DMA and DMF molecules, respectively, in liquid state. It is found that in solid state DMF molecules build very weak hydrogen bonds with each other, where formyl group CH acts as hydrogen bond donating site [1]. Being very weak, it is assumed (without proof) in our previous paper on DMF–water system [2], that DMF molecules does not mutually interact by hydrogen bonding. In the case of DMA molecule, which contains CH_3 group in formyl position, this possible hydrogen bonding site is also excluded. Thus, DMA is expected to represent the simplest system, regarding to hydrogen bonding, in the series of amides. For DMA, to our best knowledge, no crystal structure is known. DMA is characterised by high dipole moment $\mu = 3.72\,\mathrm{D}$ [3] and moderate relative static permittivity $\varepsilon_{\mathrm{r}} = 37.78$, which are both very close to that for DMF. Also, boiling points (t_{bp}=1661 °C for DMA and 153.1 °C for DMF, respectively) and vaporisation enthalpy at 25° ($\Delta_{\mathrm{vap}}H = 50.24\,\mathrm{kJ\,mol^{-1}}$ for DMA and 46.89 $\mathrm{kJ\,mol^{-1}}$ for DMF, respectively) are very similar to molar mass ratio of DMF and DMA, respectively. Yet these simple comparison of the two species show that their structure in liquid state must be very similar. However, their viscosities are significantly different ($\eta = 1.972$ mPa s for DMA and 0.794 mPa s for DMF, respectively) [3]. This is significance that some difference between the two liquids still exist.

The purpose of this study is to compare behaviour of two, at the first sight similar liquids, DMA and DMF. In order to exclude competition of solute solute and solute-solvent intermolecular interactions, carbon tetrachloride, as inert liquid miscible with both DMF and DMA in the whole composition range, was chosen.

Infrared (IR) spectroscopy provides a unique insight into hydrogen bonding. The bands in IR spectra represent vibrational modes of the molecular system under consideration. Hydrogen bonding causes prominent changes in bands which correspond to vibrations of groups directly involved in hydrogen bond. However, experimental IR spectra contain also apparent absorption, caused by optical effects due to experimental setup. Thus, experimental IR spectra need additional workup in order to extract these effects. Complex optical constant spectra $n(\widetilde{\nu})$ and $k(\widetilde{\nu})$ reflect influence of the sample itself to applied infrared radiation. In the other words, these spectra are free from all artifacts due to the experimental optics [4]. So, they provide insight into molecular properties of the sample. Accordingly, molar absorption coefficient spectrum $\varepsilon(\widetilde{\nu})$, by

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Table 1
Sample preparation. Masses are given in mg.

Sample	$m_{\mathrm{CCl_4}}$	m_{DMA}	x_{DMA}	Sample	$m_{\mathrm{CCl_4}}$	m_{DMA}	x_{DMA}
1	7.72511	0.22548	0.04901	11	4.64303	3.29244	0.55595
2	7.75740	0.45017	0.09294	12	3.07853	2.70556	0.60811
3	6.15484	0.58357	0.14340	13	3.15035	3.31500	0.65009
4	6.28970	0.90832	0.20317	14	3.09644	4.15476	0.70318
5	6.25358	1.21680	0.25570	15	1.44393	2.72018	0.76885
6	6.27691	1.52995	0.30087	16	1.49677	3.55313	0.80737
7	5.59638	1.70754	0.35011	17	1.42826	6.48427	0.88908
8	5.48546	2.17939	0.41228	18	0.81178	3.99473	0.89679
9	5.46518	2.54022	0.45075	19	0.35640	8.49968	0.97680
10	4.66257	2.64879	0.50076	20	0	5	1

Table 2
Spectral regions used to measure optical constants. T states for transmission, while MRA and SRA state for multiple- and single-reflection ATR technique, respectively. Spectral ranges are given in cm^{-1}.

Spectra	R1 5000–3225	R2 3240–2620	R3 2635–1855	R4 1870–1305	R5 1315–850
1–3	T	T	T	SRA	MRA
4–12	T	MRA	T	SRA	MRA
13–20	T	MRA	T	SRA	SRA

Table 3
Linear absorption coefficients $K(\tilde{\nu})$ at anchor points for DMA–carbon tetrachloride mixtures. Refraction indices used to determine linear coefficients are those obtained by fitting of experimental data, as listed in Table 4. Numbers in the first line represent the corresponding sample, as given in Table 1.

$\tilde{\nu}$ (cm^{-1})	$K(\tilde{\nu})$ (cm^{-1})						
	1	4	7	10	13	16	20
4990.0	0.4548	0.4623	0.4495	0.4501	0.4555	0.4601	0.4495
4850.0	0.4493	0.4504	0.4510	0.4404	0.4482	0.4511	0.4505
3750.0	0.4678	0.6622	0.8475	1.0374	1.2257	1.4240	1.6668
3360.0	0.6090	3.2019	5.2279	6.8538	8.0147	8.7520	8.9766
3228.0	0.8863	3.2379	5.4792	7.7772	10.055	12.454	15.393
2635.0	0.6140	2.3148	3.9358	5.5977	7.2452	8.9803	11.105
2331.7	1.0827	1.8472	2.5758	3.3229	4.0634	4.8433	5.7986
2036.3	0.5919	1.1588	1.6991	2.2530	2.8021	3.3804	4.0887
1870.0	0.8159	1.6846	2.5125	3.3613	4.2027	5.0889	6.1742

its IUPAC definition [5], must be determined from absorption index $k(\tilde{\nu})$ (imaginary part of complex index of refraction). From optical constants, one can also readily calculate dielectric constant (ε' and ε'') and molar polarisability (α'_m and α''_m) spectra [6]. Intensity of the bands in $\tilde{\nu}\alpha''_m$ spectra are directly proportional to fundamental spectroscopic quantities, vibrational transition moment $|\vec{R}_j|$ and dipole moment derivatives μ_j with respect to normal coordinate [6]. Accordingly, there is a great interest in accurate determination of optical constants. In a series of papers accurate methods for determination of optical constants of liquids in the mid-infrared region, for spectra obtained by both transmission [4,7,8] and attenuated total reflection (ATR) [9] are reported.

Until now, optical constants were reported for a number of neat liquids [10–27]. Regarding liquid mixtures, by our knowledge, only optical constants for aqueous mixtures of acetonitrile [28] and DMF [2] are reported.

This is the first paper in the scheduled series. Here the concentration is addressed to measurement of optical constants and derived quantities (molar absorption coefficients, dielectric constants, molar polarisabilities, transition moments and dipole moment derivatives) in the mid-infrared region of the spectrum (from 5000 to 850 cm^{-1}) of DMA–carbon tetrachloride mixtures over the whole composition range. This will be the basis for any further discussion of the system, regarding DMA–DMA intermolecular interactions in the liquid state.

Table 4
Refraction indices of DMA–carbon tetrachloride mixtures.

x_{DMA}	n^{D}[a]	$n^{\mathrm{D}}_{\mathrm{fit}}$[b]	x_{DMA}	n^{D}	$n^{\mathrm{D}}_{\mathrm{fit}}$
0.0490	1.4575	1.4574	0.5560	1.4510	1.4508
0.0929	1.4572	1.4573	0.6081	1.4498	1.4494
0.1434	1.4570	1.4570	0.6501	1.4487	1.4483
0.2032	1.4563	1.4566	0.7032	1.4467	1.4468
0.2557	1.4559	1.4561	0.7688	1.4440	1.4447
0.3009	1.4555	1.4555	0.8074	1.4430	1.4434
0.3501	1.4546	1.4548	0.8891	1.4405	1.4404
0.4123	1.4539	1.4538	0.8968	1.4400	1.4401
0.4507	1.4532	1.4531	0.9768	1.4370	1.4368
0.5008	1.4520	1.4520	1.0000	1.4359	1.4358

[a] Experimentally obtained data.

[b] Refractive indices obtained by fitting the experimental data to second-order polynomial.