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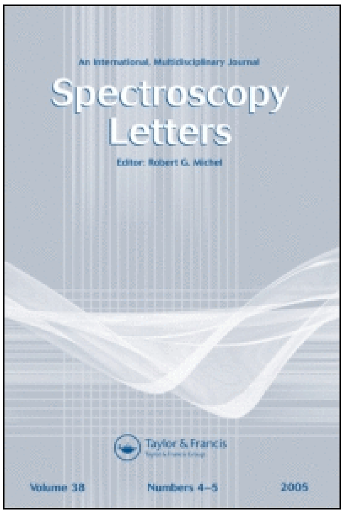

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MOLECULAR CONTACT COMPLEXES OF AMIDES AND OXYGEN

Key words: Contact complex, Charge-transfer absorption, Oxygen, *N,N*-dimethylformamide, *N,N*-dimethylacetamide

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Abstract

Contact transfer charge (CCT) absorption spectra of *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMA) with molecular oxygen (O_2) have been investigated. These solvents form contact complexes with O_2 and have strong ultraviolet CCT absorption bands with intensities that are related to the partial pressure of the applied O_2 and the mole percentages of DMF and DMA in DMF/acetonitrile (MeCN) and DMA/MeCN mixtures, respectively. Electron spin resonance spectra and luminol chemiluminescence tests confirm the absence of the formation of superoxide ions from oxygenated DMF and DMA solutions.

Introduction

N,N-Dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMA) are widely used dipolar aprotic solvents for many organic and inorganic compounds in which an aprotic solvent environment is necessary because of their fairly high relative permittivity [1,2]. The properties of aqueous mixtures of DMF and DMA have received considerable attention in the past years. Some studies including dielectric constants [3,4]; enthalpies of dilution [5]; conductance of electrolytes in aqueous mixtures of DMA [6]; magneto-optical rotation [7]; NMR; densities; viscosities [4,8]; diffusion; refractivity [8]; and limiting partial molar volumes of electrolytes in aqueous mixtures of DMF [9] have been made in order to elucidate the mechanism of the interaction of ion-solvent and solvent-water interactions.

It has been known that some organic solvents exhibit contact charge transfer (CCT) absorption with molecular oxygen (O_2) [10]. Molecular O_2 acting as an electron acceptor via its triplet electronic state ($^3O_2$) can form a donor-acceptor ($D\cdots{}^3O_2$) contact pair with some solvents acting as electron donors. Radiation absorbed by the ground state $D\cdots{}^3O_2$ contact pair gives an excited state $(D\cdots{}^3O_2)^*$ which subsequently dissipates the excess energy through one or more mechanisms [11,12]. However, studies of the contact complexes of DMF and DMA with O_2 have not been received much attention although these solvents are widely used in organic synthesis and analytical spectroscopy. The work described here is to report the CCT absorption of DMF and DMA with O_2. The results can provide an insight of the interaction of these solvent molecules with dissolved O_2 molecules.

Materials and Experimental

DMF (99.9 %, HPLC grade), DMA (>99.9 %, HPLC grade) and acetonitrile (MeCN, >99.9 %, HPLC grade) were purchased from Aldrich Chemical Co. Ltd., England. Luminol (>98 %) was from Fluka Chemicals, England. 'White spot' nitrogen (N_2) gas (O_2 free), O_2, carbon dioxide (CO_2) and hydrogen (H_2) gases were supplied by BOC Ltd., England.

Different oxygen concentrations [O_2] (in the range 0 to 100 %) in the gas stream were produced by controlling the flow rates of O_2 and a diluent N_2 gas entering a mixing chamber. The gas mixture from the chamber passed through a portable O_2 meter (Oxywarn 100I from Draeger Manufacturing, England) where the [O_2] in the gas mixture was determined before passing through the solvent contained in a 10 mm path-length spectrophotometer silica cuvette.

The ultraviolet (UV) absorption spectra were measured on a Perkin-Elmer Lambda 15 spectrophotometer (Perkin-Elmer, England) equipped with a Epson FX-850 dot-matrix printer (Epson Telford, England) using silica cuvettes of 10 mm path-length. Background corrections for the UV absorption spectra were done by filling the reference beam cuvette in the spectrophotometer with the corresponding solvents saturated with air. Gaseous standards with different [O_2] values at flow rates of about 30 cm^3/min passed through the solvent until it was totally gas saturated and the UV absorption spectrum was recorded as soon as possible. The CCT absorption spectra for different mole percentage solvent mixtures of DMF/MeCN and DMA/MeCN were also recorded. Electron spin resonance (ESR) spectra of oxygenated DMF and DMA solutions were recorded on a Bruker EPR 300E spectrometer at 77 K.

Results and Discussion

The CCT absorption spectra of DMF and DMA with O_2 are shown in Figs. 1 and 2, respectively. The absorption bands are broad and lie mainly in the UV region. The absorption bands disappear when the dissolved O_2 in the solvents are removed by purging with N_2, CO_2 or H_2 gases and they re-appear when the solvents

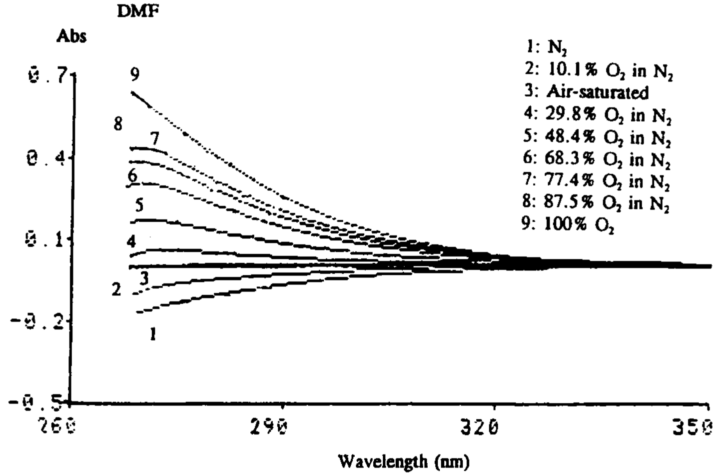


Fig. 1
The effect of different oxygen concentrations on the CCT absorption spectra of DMF. The optical path-length of cuvette is 10 mm and the reference is air-saturated DMF.

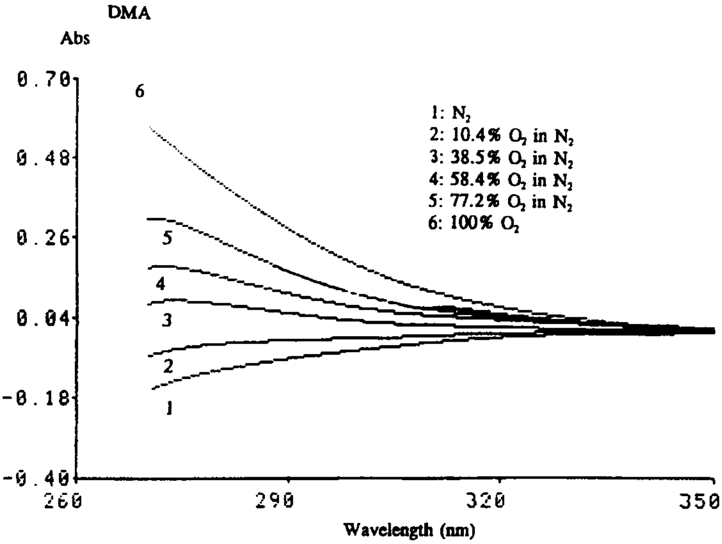


Fig. 2
The effect of different oxygen concentrations on the CCT absorption spectra of DMA. The optical path-length of cuvette is 10 mm and the reference is air-saturated DMA.

are passed through with O_2 again. A negative absorption band is observed for the solvents with $[O_2]$ less than the atmospheric concentration (~ 21 % (v/v)) as the reference cell contains air-saturated solvent. The CCT absorption band maxima could not be determined accurately and reliably in the region under 270 nm because of the overlap of the continuous bands with the very much stronger absorption band of the solvent itself. The apparent maxima for the CCT absorption bands will be distorted because of the stray light effect of the solvents in the shorter wavelength region. Spurious absorption maxima often arise in solvents having very intense absorption bands [13].

The effect of $[O_2]$ on the CCT absorption intensity is shown in Fig. 3 with plots of A_{O2} at a wavelength of 280 nm against applied $[O_2]$ in the solvents where in this case, A_{O2} = absorbance of solvent saturated with O_2 standards — absorbance of solvent saturated with N_2 (i.e. $[O_2] = 0$ %). The graphs show that the CCT absorbance at this wavelength increases linearly with $[O_2]$. The wavelength of 280 nm was chosen as they are far away enough from the maximum of the solvent absorption band for there to be any instrumental errors as described earlier. Similar straight line graphs are obtained when other wavelengths in the CCT absorption bands are used with plots of A_{O2} against $[O_2]$ having a steeper slope for wavelengths nearer the maximum of the absorbance peak for the CCT spectrum. These results show that the CCT absorption spectra of the solvents with O_2 obey Beer-Lambert's law.

The effect of the concentration of DMF and DMA in solvent mixtures of DMF/MeCN and DMA/MeCN on the CCT absorption spectra is shown in Figs. 4 and 5, respectively. Acetonitrile was used as the co-solvent due to its light transparency and absence of CCT absorption bands in the wavelength region used in the investigation [11]. All the solvent mixtures investigated were saturated with pure O_2.

It is found that the absorption intensity of the CCT absorption bands of the solvent mixtures with O_2 decreases as the concentration of DMF and DMA in solvent mixtures of DMF/MeCN and DMA/MeCN diminishes. Plots of A_{O2} at 280 nm against mole % of DMF and DMA in MeCN (Fig. 6) show fairly linear straight lines that indicate the absorption intensity is related to the concentration of DMF and DMA in the solvent mixtures of DMF/MeCN and DMA/MeCN, respectively. Since all the solvent mixtures were saturated with pure O_2, the actual concentration of dissolved O_2 in each mixture probably varies according to the composition of the mixture because of the difference in the solubilities of O_2 in DMF, DMA and MeCN. This effect causes a slight non-linearity of the lines shown in Fig. 6.

A donor molecule (D) reacts with an O_2 molecule to form a molecular contact complex $D\cdots O_2$ which is responsible for the CCT absorption as follows [12]:

$$D + O_2 \rightleftarrows D\cdots O_2 \overset{h\nu}{\rightleftarrows} (D\cdots O_2)^* \qquad (1)$$

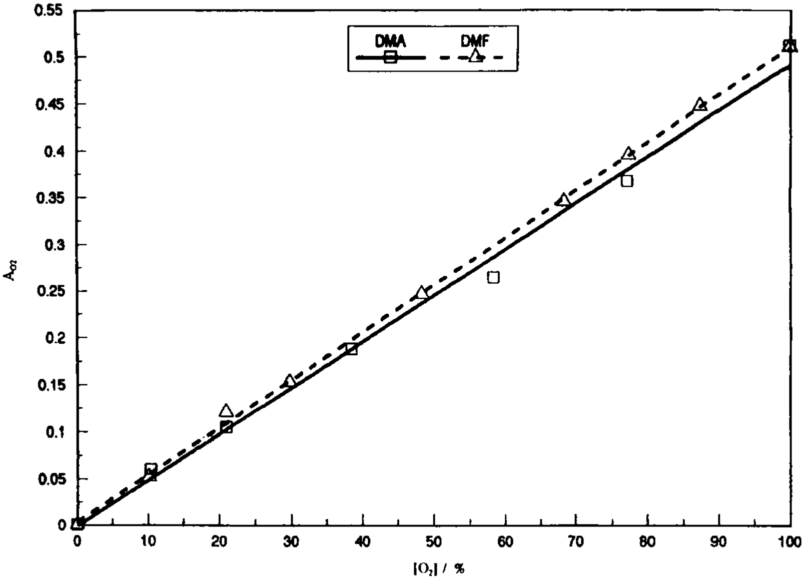


Fig. 3
Plot of A_{O2} against $[O_2]$ at 280 nm using the data from Figs. 1 and 2.

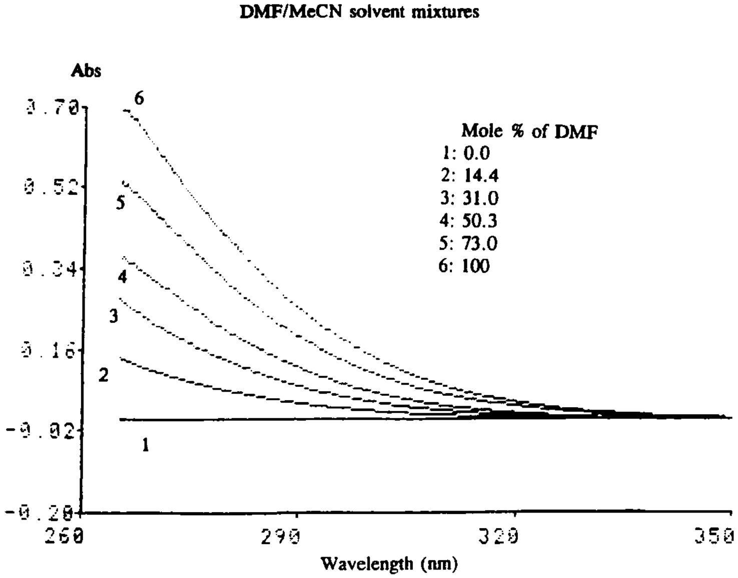


Fig. 4
The CCT absorption spectra of DMF/MeCN solvent mixtures. Solvent mixtures are in mole percentages.

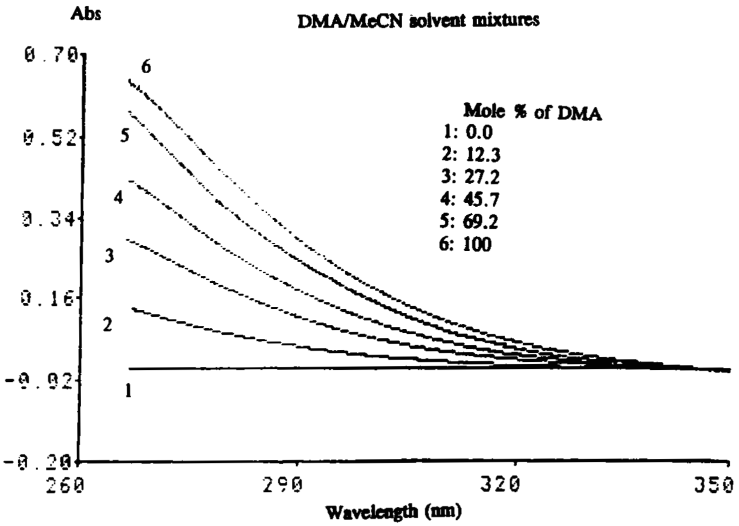


Fig. 5
The CCT absorption spectra of DMA/MeCN solvent mixtures. Solvent mixtures are in mole percentages.

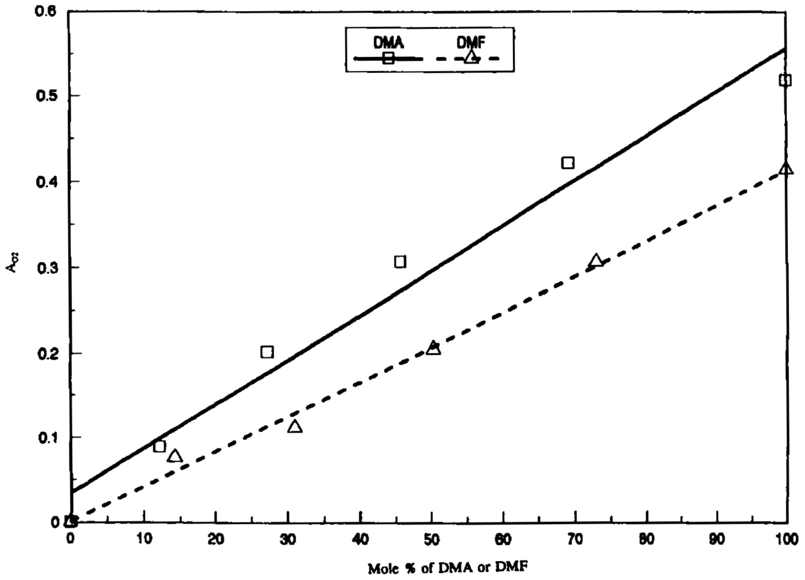
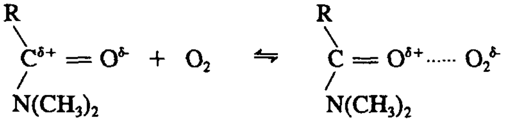


Fig. 6
The effect of different solvent concentrations on the CCT absorption of DMA and DMF. Plots of A_{O2} against Mole % of DMA or DMF in MeCN at 280 nm using the data from Figs. 4 and 5.

$$A_{O2} = K[D]P_{O2} \quad (2)$$

where A_{O2}, K, [D] and P_{O2} are the CCT absorbance, a constant, the mole fractions of donor (in this case, DMF or DMA) and the partial pressure of the applied O_2, respectively. It is obvious that DMF and DMA follow the aforementioned equations as donors in the CCT process with O_2.

Luminol chemiluminescence tests and ESR spectra confirmed the absence of the formation of superoxide ions in oxygenated DMF and DMA solutions. It has been reported that iodine (electron acceptor) can form adducts with amides (electron donors) [14]. Likewise the mechanism for the CCT of amides with O_2 is that a contact complex is first formed between amides and O_2 molecules with the partial transfer of an electron from the carbonyl oxygen in the amide molecule to the O_2 molecule:



(3)

where R = H or CH_3

It is the absorption of a UV photon by the contact complex which gives rise to the CCT absorption spectra for amides with O_2.

REFERENCES

1. Juillard J. Dimethylformamide. In Coetzee J.F., ed. *Recommended Methods for Purification of Solvents and Tests for Impurities*. Oxford : Pergamon Press Ltd. 1982: 32-37.

2. Vaughn J.W. Amides. In: Lagowski J.J., ed. *The Chemistry of Non-aqueous Solvents*. London : Academic Press Inc. 1967, vol. II : 237-264.

3. Rohdewald P.; Moldner M. Dielectric Constants of Amide-Water Systems. J. Phys. Chem. 1973; 77: 373-377.

4. Kinart C.M.; Kinart W.J.; Skulski L. Study on the Structure of Aqueous Solutions of Formamide, Methylformamide and Dimethylformamide by means of Measuring their ^{1}H NMR Spectra, Densities, Viscosities and Relative Dielectric Permittivities. Pol. J. Chem. 1985; 59: 597-603.

5. Wood R.H.; Hiltzik L.H. Enthalpies of Dilution of Aqueous Solutions of Formamide, Acetamide, Propionamide, and *N,N*-Dimethylformamide. J. Solution Chem. 1980; 9: 45-57.

6. Bahadur L.; Ramanamurti M.V. Conductance Studies in Amide+Water Mixtures. J. Chem. Soc. Faraday 1 1980; 76: 1409-1418.

7. Dawber J.G. Magneto-optical Rotation Studies of Liquid Mixtures. J. Chem. Soc. Faraday Trans. 1 1982; 78: 1127-1130.

8. Volpe C.D.; Guarino G.; Sartorio R.; Vitagliano V. Diffusion, Viscosity, and Refractivity Data on the System Dimethylformamide-Water at 20 and 40 °C. J. Chem. Eng. Data 1986; 31: 37-40.

9. Garcia-Pañeda E.; Yanes C.; Calvente J.J.; Maestre A. Limiting Partial Molar Volumes of Electrolytes in Dimethylformamide-Water Mixtures at 298.15 K. J. Chem. Soc. Faraday Trans. 1994; 90: 575-577.

10. Evans D.F. Molecular Association of Oxygen and Aromatic Substances. J. Chem. Soc. 1953: 345-347.

11. Tsubomura H.; Mulliken R.S. Molecular Complexes and their Spectra. XII. Ultraviolet Absorption Spectra Caused by the Interaction of Oxygen with Organic Molecules. J. Am. Chem. Soc. 1960; 82: 5966-5974.

12. Onodera K.; Furusawa G.-I.; Kojima M.; Tsuchiya M.; Aihara S.; Akaba R.; Sakuragi H.; Tokumaru K. Mechanistic Considerations on Photoreaction of Organic Compounds via Excitation of Contact Charge Transfer Complexes with Oxygen. Tetrahedron 1985; 41: 2215-2220.

13. Evans D.F. Spurious Maxima at Long Wavelengths in Ultra-violet Absorption Spectra. Chemistry and Industry 1953: 1061.

14. Drago R. S.; Wenz D.A; Carlson R.L. Thermodynamic Data for Iodine Adducts with a Series of Substituted N,N-Dimethylamides. J. Am. Chem. Soc. 1962; 84: 1106-1109.

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