J Incl Phenom Macrocycl Chem
DOI 10.1007/s10847-007-9360-x

ORIGINAL ARTICLE

NMR and photo-CIDNP investigations of the glycyrrhizinic acid micelles influence on solubilized molecules

V. S. Kornievskaya · A. I. Kruppa · T. V. Leshina

Received: 14 May 2007 / Accepted: 28 July 2007

Abstract It was found that photolysis of *N*-acyl anthranilic acid methyl ester is very sensitive to solvent nature. This sensitivity was connected with the equilibrium between intramolecular and intermolecular hydrogen bonding. Also it has been established the glycyrrhizinic acid micelle formation in water-methanol mixture with CMC about 0.5–1 mM. Solubilization of *N*-acyl anthranilic acid methyl ester in glycyrrhizinic acid micelles decreases photoreaction efficiency comparing with the homogeneous solvent.

Keywords Glycyrrhizinic acid · Micelles · β-cyclodextrin · Host-guest complex · T2 relaxation · Mechanism of photolysis of *N*-acyl anthranilic acid methyl ester

Abbreviations

AM1 UHF	Unrestricted Hartree-Fock semi-empirical quantum chemical calculation method
CIDNP	Chemically Induced Dynamic Nuclear Polarization
CMC	Critical Micelle-Formation Concentration
CPMG	Carr-Parcel-Meiboom-Gill pulse sequence used to investigate the spin-spin relaxation in NMR
EPR	Electron Paramagnetic Resonance Spectroscopy
HFC	Hyperfine Coupling Constant
GA	Glycyrrhizinic acid
NMR	Nuclear Magnetic Resonance Spectroscopy
MA3	*N*-acyl anthranylic acid methyl ester
MAR	2-(carboxymethyl phenyl) aminyl radical
T_2	Nuclear spin-spin relaxation time

V. S. Kornievskaya · A. I. Kruppa (✉) · T. V. Leshina
Institute of Chemical Kinetics and Combustion, Siberian Branch of Russian Academy of Sciences, Institutskaya str. 3, Novosibirsk 630090, Russian Federation
e-mail: kruppa@kinetics.nsc.ru

Introduction

Glycyrrhizinic acid (GA) is the object of investigation for many researchers for some reasons: the biologically specific GA and its derivatives are widely spread [1, 2], also it has been long known to possess antiviral activity, antitumour, antidiabetic and other useful properties [3, 4].

The ability of GA to modify the properties of other medicines has been assigned to complexing [5–7], which, however, has no physicochemical foundation. In the literature, the opinion was put forward that at low concentrations the cyclic dimeric structures can be formed in GA through intermolecular hydrogen bonds possessing a hydrophobic cavity [8]. The existence of the cavity provides a way for the formation of host-guest complexes typical of, e.g., cyclodextrin [9]. On the other hand, the presence of both the hydrophobic (triterpene fragment) and hydrophilic (two gluocoronide residues) parts (Fig. 1) allows the assumption that GA and its derivative can form micelles in certain conditions in both water and water-alcohol solutions [7]. The recent physicochemical studies on the interaction between GA and such medicines as nifedipine and lapaconitine in water-alcohol solutions allowed us to reveal the existence of the aggregates of GA with medicinal molecules with stoichiometry 2:1 in the GA concentration range of 10^{-3}–10^{-5} M [10]. The two steps observed in the curve of the dependence of nifedipin solubility on GA concentration in solution

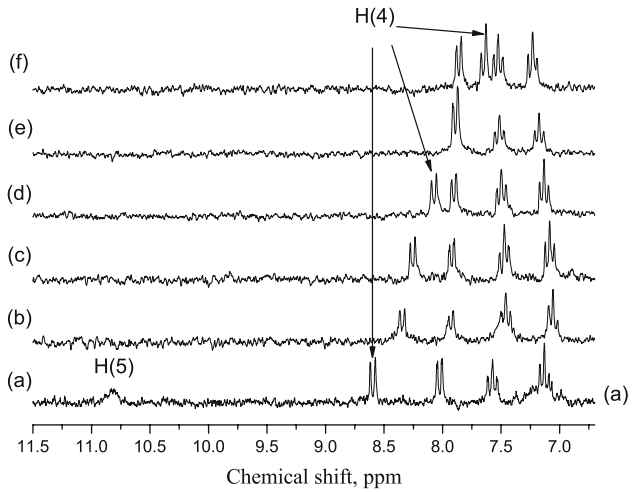


Fig. 1 ^{1}H NMR spectra of 1 mM MA3 in various solvents: (**a**) in CD_3CN; and in D_2O/CD_3OD mixtures with different water volume fraction φ: (**b**) 0, (**c**) 0.1, (**d**) 0.3, (**e**) 0.5, (**f**) 0.8. Arrows indicates signals of H(4) protons of MA3

indicate phase transitions which made the authors [11] to assume the existence of the two types of associates: a complex and a micelle. In these works, however, there is no information on the composition of associates. Therefore, it is stated that at present, the problem of the origin of associates, formed by GA with biologically active compounds, is not solved. In addition, the authors of this work think it important to get information on the fact whether GA solutions are "true solutions, gels, or micelles.

Thus, the goal of this work is to use one of the most popular experimental methods for studying supramolecular structures, namely, NMR spectroscopy, to investigate a possible association of GA both in solutions and upon interaction with organic molecules. The Chemically Induced Dynamic Nuclear Polarization (CIDNP) method, well-known to be rather productive for studying radical processes [12], was used in combination with other methods to study in detail both the structure of micelles [13] and their effect on the reactivity of solubilized compounds [14]. Recently, it has been also used to study the influence of host-guest complexes with β-cyclodextrin on the reactivity of the compounds included [15]. In the present work, the combination of NMR and CIDNP methods is used to investigate GA associations and to establish its influence on the photolysis of *N*-acyl anthranylic acid methyl ester. In particular, it has been studied both the influence of the nearest environment of the nuclei of GA and ester on their chemical shifts and the change in the of the nuclear relaxation times of GA nuclei upon formation of a supramolecular structure over the concentration range in which the GA micellization has been assumed [11].

Experimental

Chemicals

Deuterated solvents D_2O(99.9% D), CD_3OD(99.5% D), cyclohexane (99.5% D) (all by Aldrich) were used without repurification. CD_3CN(99.8% D) (Izotop) was preliminarily distilled above P_2O_5 to remove remaining water and various impurities. GA and *N*-acyl anthranylic acid methyl ester (MA3) were kindly donated by Prof. Salakhutdinov (Institute of Organic Chemistry SB RAS, Novosibirsk). The mechanism of MA3 photolysis was studied using both individual solvents and D_2O/CD_3OD mixtures of various water volume fraction (φ). To study GA associations and its influence on MA3 photoreaction, the D_2O/CD_3OD mixture with $\varphi = 0.8$ was used.

Experimental methods and equipment

All NMR experiments (including photo-CIDNP and the measurement of relaxation times) were performed using an NMR Bruker DPX200 spectrometer supplied with a photoprobe and a temperature adapter. An excimer Lambda Physics EMG101 (XeCl, 308 nm, 100 mJ) laser was used as a light source. The coefficient of energy transfer from the laser to a sample was, for our experimental set-up, in the range of 25%. Relaxation times were measured at 25°C. The experiments on photo-CIDNP were carried out at room temperature. The photo-CIDNP was recorded using both the time-resolved [16] and quasi-stationary [17] variants of pulse trains. The T_2 relaxation was measured by means of a Carr-Parcel-Meiboom-Gill (CPMG) sequence of the type: $p(90°)-(\tau-p(180°)-\tau)_n-$acquisition, where $\tau = 2$ ms, and n was varied from 0 to 4028 [18].

Sample preparation

The MA3 concentration was 1 mM in all experiments. The GA concentration was varied from 0.2 mM to 2.5 mM. The GA solutions were prepared according to the following scheme: first, GA was dissolved in CD_3OD and then D_2O was added to a volumetric ratio of φ. To reach equilibrium upon association the GA solutions were heated to 50°C and mixed up using a magnetic stirrer for several hours. All NMR samples were bubbled by argon for 15 min just before an experiment.

Quantum chemical calculations

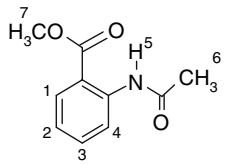
The estimation of signs of hyperfine coupling constants in radical intermediates was made by using the HyperChem

v.7 (Hypercube Inc.). Calculations were performed by AM1 UHF method by the next sequence: firstly, a geometry optimization and then single point calculation to evaluate the sign of spin densities at protons under study.

Results and discussion

The study of MA3 photolysis mechanism

Since the aim of the present study was to determine the influence of GA association on the reactivity of molecules included in associates, the first problem was to choose the compound whose reactivity depends substantially on the environment of a given compound. The *N*-acyl anthranilic acid methyl ester (MA3) was taken as this compound.



MA3

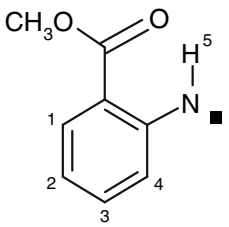
First, it was established that the chemical shifts of MA3 aromatic protons change substantially in the NMR spectrum depending on the medium used. Figure 1 shows the NMR spectra of MA3 in various solvents.

As follows from the Fig. 1 the transition from acetonitrile and methanol to water, causes a substantial change in the NMR spectrum: (1) the narrowing of the range of chemical shifts of aromatic protons; and (2) the signal of H(5) proton is observed only in acetonitrile.

The position of the H(5) wide line in the range of 10.8 ppm (Fig. 1a) unambiguously indicates the appearance of the intramolecular hydrogen bond between NH and carboxyl group oxygen in the MA3 molecule, which can lead to the formation of energetically advantageous six-membered cycle. In other solvents this signal is unobservable due to the participation of NH group in the exchange processes with the hydroxyl protons of methanol and water protons. On the other hand, the observed narrowing in the range of the chemical shifts of MA3 aromatic protons with increasing water content in a solution testifies to a change in the electron density distribution in an aromatic ring. Chemical shifts of H(4) protons are most sensitive to used media. It is assumed that these changes can be assigned to the shift of equilibrium toward the MA3 structure in which the intramolecular hydrogen bond is replaced by the intermolecular one with solvent molecules with an increase in water concentration. A similar assumption was made previously for parent 2-amino-acetophenone and its derivations including 2-acetamido-acetophenone [19]. Moreover it was found that shift from intramolecular to intermolecular hydrogen bonding drastically affects on photophysical properties of 2-acetamido-acetophenone [19]. It allows to propose the same influence on photochemical activity of MA3 with varying of water content in water-methanol mixture.

In fact the changes in NMR spectrum are accompanied by the change in the reactivity of MA3 upon its photolysis in solutions. Thus, photo-CIDNP is not observed during irradiation of MA3 solutions in acetonitrile. At the same time, the nuclear polarization is observed in D_2O/CD_3OD mixtures which indicates the radical decay of MA3. Figure 2 shows the photo-CIDNP spectra in D_2O/CD_3OD mixtures.

The chemical polarization is registered on both aromatic protons and the protons corresponding to those of the acyl group. The main polarization in the region of aromatic protons is observed at the initial compound whose intensity (as follows from Fig. 2) depends substantially on the solvent used. In this case, the presence of several polarized different products, containing an acyl fragment, indicates a homogeneous decay of MA3 in the reaction of photo-deacylation. The aminyl radical (MAR), resulting from MA3 photo-decay, is sure to be the partner of the acetyl radical in a radical pair.



MAR

To analyze polarization one should know the magnetic-

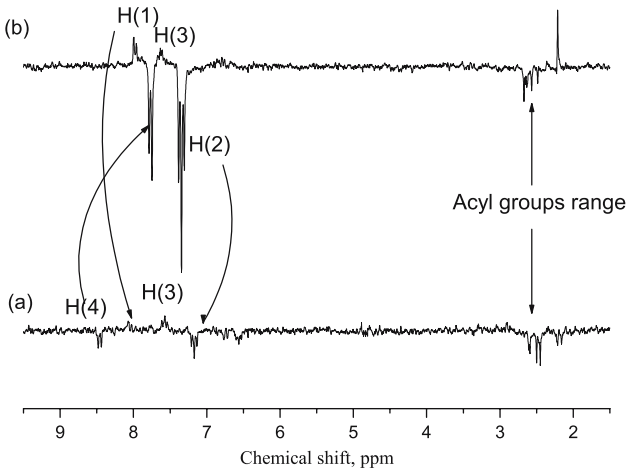


Fig. 2 ^{1}H photo-CIDNP spectra of 1 mM of MA3 in D_2O/CD_3OD mixtures with φ: (**a**) 0 and (**b**) 0.8

resonance parameters of radicals in a pair. For the acetyl radical these parameters are well known [20], whereas the attempts to find parameters of MAR radical EPR spectrum was failed. Nevertheless the values of magnetic-resonance parameters of parent 2-(carboxyphenyl) aminyl radical are known: g = 2.00345, a(1) = 0.210 mT, a(2) = 0.811 mT, a(3) = 0.182 mT, a(4) = 0.627 mT [21]. One might assume that additional methyl group cannot change drastically the spin density distribution in MAR comparing to 2-(carboxyphenyl) aminyl radical. Follows to CIDNP theory the ratio of the polarization intensities of different protons of MA3 should be close to ratio of hyperfine coupling constants (HFC) values of the same protons in MAR. The expected ratio is 1.15:4.45:1:3.44 which is close to experimental ratio of 1.4:6.8:1:3.4 for 1–4 protons positions, respectively. That indicates that assumptions of MAR as intermediate in radical process is righteous. The signs of HFC were estimated using semi-empirical quantum-chemical calculations (UHF AM1). Table 1 summarizes the calculated HFC signs of the MAR radical and the experimental signs of the polarization of corresponding protons at the initial MA3.

Table 1 HFC signs at aromatic protons of MAR and CIDNP signs of MA3

Proton position	1	2	3	4
HFC sign	+	−	+	−
CIDNP sign	+	−	+	−

As follows from the Table 1, the CIDNP signs at the initial MA3 correspond to spin density distribution in the aminyl radical resulting from MA3 photo-deacylation. The value of g(MAR) should be near to the same of 2-(carboxyphenyl) aminyl radical, whereas g(CH_3CO) = 2.0005 [20]. Therefore, at $g > 0$, according to the existing rules [12, 22], the polarization signs observed at the product of the geminate recombination (initial MA3) corresponds to the photo-decay from the triplet state. The mechanism of photolysis describing the polarization observed can be represented as (Fig. 3)

Another interesting peculiarity of the system under study is a symbate change in both CIDNP intensity and the chemical shifts of corresponding protons with increasing water volume fraction in mixture solution. The dependence of both the relative changes in the chemical shift of the H(4) proton and the relative intensity of its polarization on water volume fraction in the D_2O/CD_3OD mixtures is demonstrated in Fig. 4.

The changes in the chemical shifts of MA3 and its reactivity upon transition from acetonitrile to water-methanol mixtures can be explained as follows. If the MA3

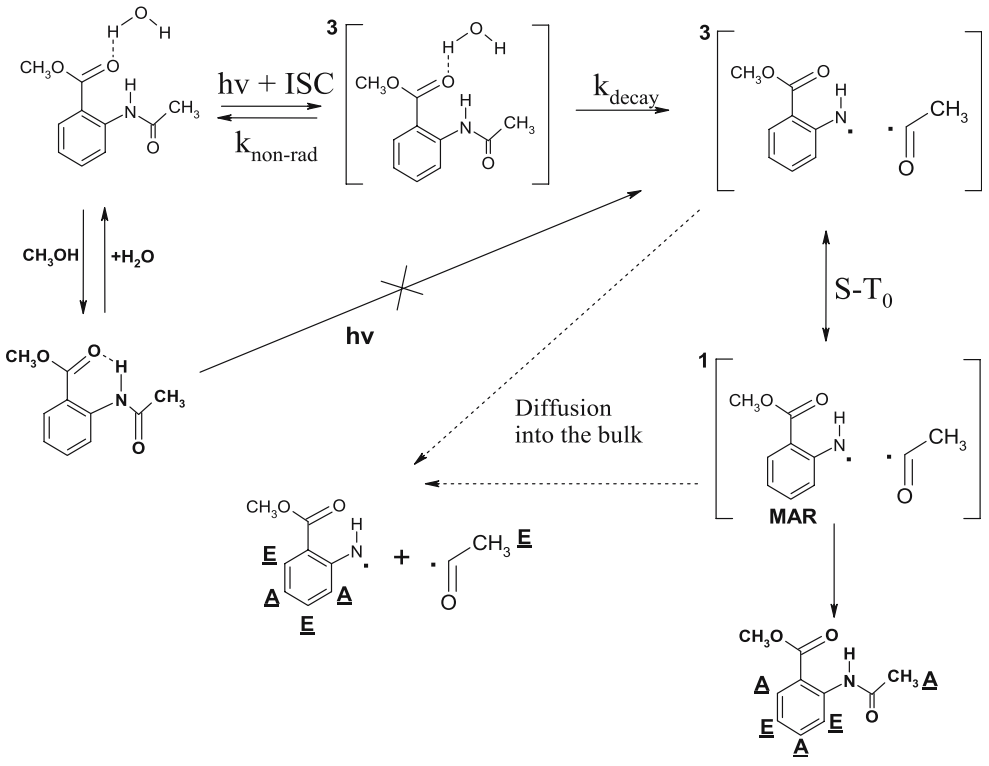


Fig. 3 The photolysis mechanism of MA3

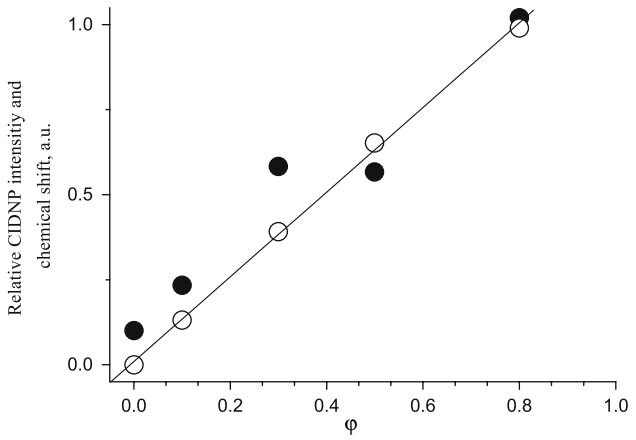


Fig. 4 Relative chemical shift (◯) of H(4) aromatic protons of MA3 and its CIDNP intensity (●) in mixture D_2O/CD_3OD as a function of water volume fraction

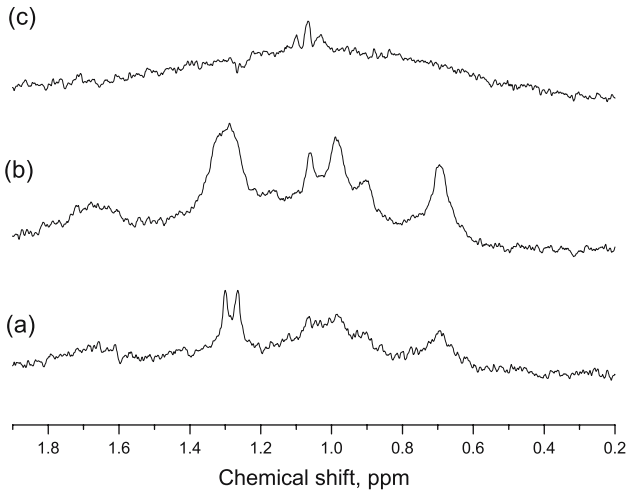


Fig. 5 ^{1}H NMR spectra of CH_3 groups of GA in the D_2O/CD_3OD (φ = 0.8) at the different concentrations GA: (**a**) 0.5 mM, (**b**) 1.0 mM, (**c**) 1.5 mM

molecule in acetonitrile solution is not subjected to photodecay due to the presence of the intramolecular hydrogen bond then in the presence of water this bond can be broken due to protonation of a nitrogen atom. In this case, an increase in D_2O concentration can cause the shift in equilibrium toward the formation of intermolecular hydrogen bonds between NH and D_2O. This unambiguously describes the tendency of changes in both chemical shifts and reactivity. The linearity of the above-mentioned changes is due to the fact that photo-decay is observed in the case of molecules bound by intermolecular hydrogen bonds only. This is in fair agreement with photophysical results of [19] where it was found extremely fast nonradiative decay of excited states of 2-amino-acetophenone derivatives in aprotic solvents and weak decay rate in protic solvents. The fast nonradiative decay prevents the photodecomposition while weak decay increases probability of photochemical reaction.

Thus, the revealed sensitivity of NMR spectra and MA3 photolysis to the effect of a medium allows us to employ MA3 as a probe for the nearest environment which can be useful for studying the formation of supramolecular structures (micelles, host-guest complexes).

The study of GA association

Figure 5 shows the NMR spectra (the methyl protons resonance region) of GA solutions with increasing GA concentration from 0.5 to 1.5 mM.

As follows from the figure, an increase in GA concentration in solution causes a substantial line broadening which is unambiguously related to the acceleration of spin-spin relaxation (T_2) of the given protons. It is known that in liquids a change in the rate of nuclear T_2 relaxation depends on the change in the rotation correlation time of the particle to which the nuclei under study belong [23]. The rotation correlation time depends, in turn, on the particle size which can vary substantially upon association of GA molecules. Therefore, in the present paper, the dependence of the T_2 relaxation rate of GA methyl protons on its concentration has been studied by pulse methods. Using, in this case, the most popular CPMG pulse sequence, it was revealed that the time-dependence of the integral intensity of echo signal is difficult to describe in terms of a single exponential decay even at very low GA concentrations of the order of 0.25 mM (Fig. 6).

At the same time, this dependence is well described by the biexponential function

$$A(t) = P_1 \cdot \exp(-t/T_{21}) + P_2 \cdot \exp(-t/T_{22})$$

In the literature there are many examples [24, 25] of observing biexponential relaxation in the studies on the association of monomeric compounds into micelles, clusters and liquid crystals, etc. Nevertheless unambiguous interpretation of the biexponential dependence of relaxation rate on time is absent. One of the most widely used explanations is related to the difference in the relaxation rates of the protons belonging to the same type and located either in an associate or at its periphery [24]. Another explanation can be assigned to the difference in the relaxation rates of the protons belonging to the same type and located in an associate and solution in the non-associate state. In this case, the relaxation times T_{21} and T_{22} refer to the protons in a solution and the associate, and P_1 and P_2 are the probabilities to find a molecule in the non-associated (mainly monomer) and associate states, respectively [25]. The latter holds for the case of slow exchange between the states [23].

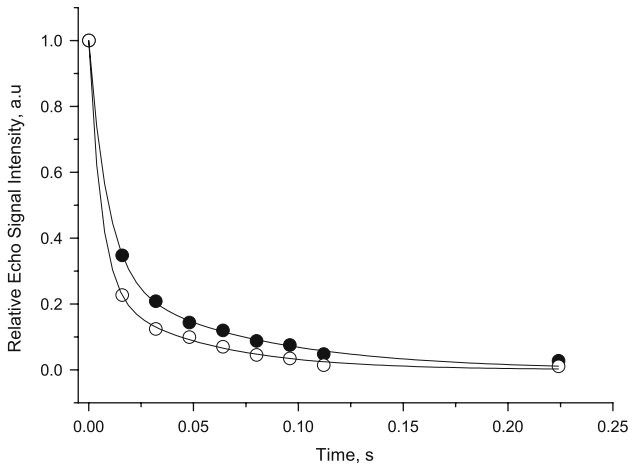


Fig. 6 Spin echo intensity dependences on time of CH_3 protons of GA at different concentrations (●) 0.25 mM and (◯) 1 mM in D_2O/CD_3OD mixture (φ = 0.8). Solid lines corresponds the best fitting curves

In our experimental conditions, a fast part of the time dependence of echo signal corresponds to the relaxation with times shorter than 10 ms. Assuming that the characteristic time of the exchange of GA molecules between the associate and solution corresponds to long times (a corresponding exchange rate being smaller than 10^2 s^{-1}), the P_1/P_2 ratio for each GA concentration can be determined. In this case, taking into account the dependence of correlation times on particle size, it is reasonable to attribute long relaxation times to molecules in solution and the shorter ones should be assigned to associates. This makes it possible to determine a change in GA molecules distribution between the non-associated and associated forms with respect to GA concentration.

Figure 7A shows the P_1 and P_2 dependences on GA concentration. Using these dependences one can easily construct the dependence of GA concentration in various forms on the initial GA concentration (Fig. 7B). The concentration of non-associated forms will describes as $[GA]_{non-Ass} = P_1 \cdot [GA]$ and that of associates as $[GA]_{Ass} = P_2 \cdot [GA]/M$ where M is the association number. Comparing (Fig. 7B) with the available literature data [25–27] indicates that the GA associates correspond to micelles when the non-associated forms are mainly present in a solution with the concentration being below the critical micelle-formation concentration (CMC), in this case about 0.5–1 mM, and above this concentration, only the micelle concentration increases whereas the concentration of non-associated forms remains practically unchanged.

Comparing the dependence of a molar fraction of GA molecules in the micellar state on the total GA concentration (Fig. 7A) with the similar dependences available in the literature [28] for various association numbers, one can conclude that GA forms micelles with small association numbers (near to 4). Indeed, these dependences are smooth and without sharp changes in a molar fraction in the CMC range only for such cases. It is worth noting that this is in agreement with the earlier assumptions of the existence to low-sized (dimeric) structures [7, 11].

The study of the influence of GA association on MA3 photo-reaction

To elucidate the influence of GA micelle-formation on MA3 photo-reaction, the ability to solubilize of MA3 in GA micelles was studied. Figure 8 shows the transformation of NMR spectrum of the aromatic protons of MA3 with increasing of GA concentration.

Comparing Figs. 8 and 2 indicates that an increase in GA concentration in the NMR spectrum causes shifts of the signals of H(4) aromatic protons of MA3 that are similar in their character to those observed with decreasing φ in

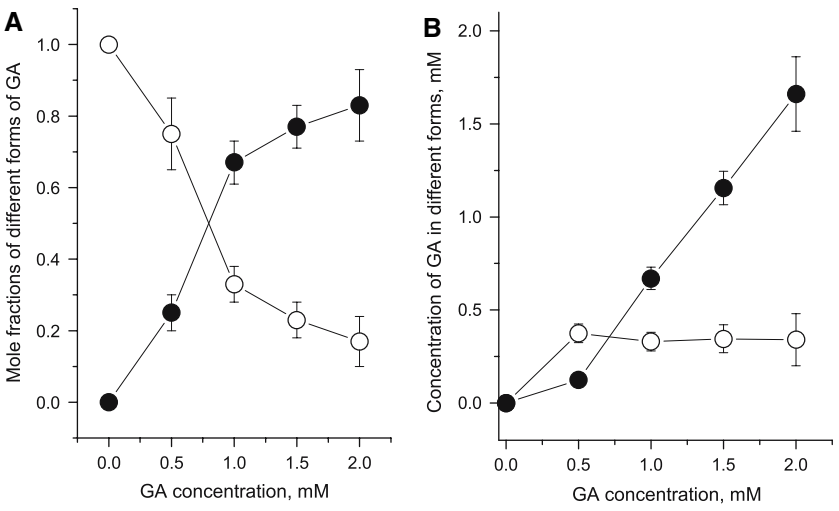


Fig. 7 (**A**) Mole fraction of associated (●—P_2) and non-associated (◯—P_1) forms of GA dependence on initial GA concentration. (**B**) Concentration of GA in associated (●) and non-associated (◯) forms of GA versus initial GA concentration

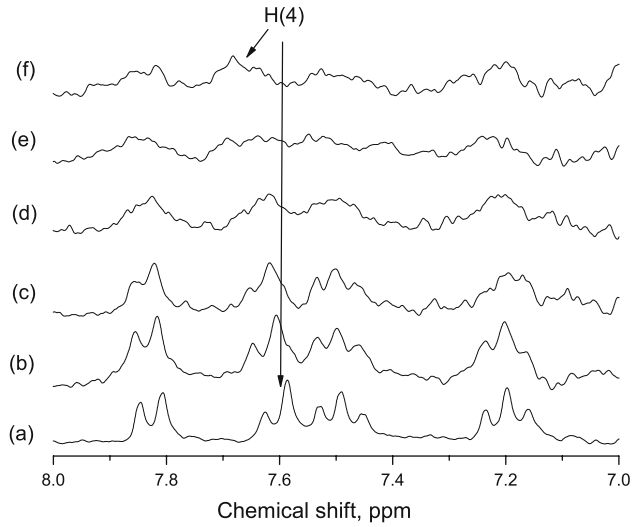


Fig. 8 ^{1}H NMR spectra of 1 mM MA3 in D_2O/CD_3OD mixture ($\varphi = 0.8$) in the presence of different GA concentrations: (**a**) 0.25 mM, (**b**) 0.5 mM, (**c**) 1 mM, (**d**) 1.5 mM, (**e**) 2 mM, (**f**) 2.5 mM. Arrows indicates H(4) proton of MA3

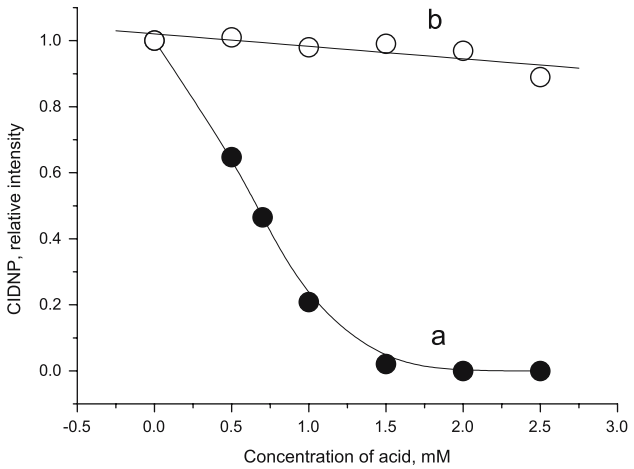


Fig. 9 CIDNP intensity dependences of aromatic protons of MA3 on (**a**) GA and (**b**) acetic acid concentrations

homogeneous D_2O/CD_3OD solutions. This is accompanied by a substantial broadening of MA3 lines (Fig. 8) which is unobservable in homogeneous solutions (Fig. 2). The latter indicates an increase in the relaxation rate of MA3 protons with increasing GA concentration (above 1 mM) which can be assigned to the fact that the MA3 molecules are involved in the micelles formed by GA. In this case, the solubilization of the MA3 molecule in the micelle on the one hand, removes water from its nearest environment which causes the shifts of lines in the NMR spectrum and on the other hand, increases the rotational correlation time of the MA3 molecule as compared with a homogeneous solution. The latter shortens relaxation times and leads to the broadening of lines in the spectrum.

Since the influence of GA on the MA3 NMR spectra due to MA3 solubilization in GA micelles was established then the influence of GA on the photochemical activity of MA3 can be studied. Figure 9a shows the dependence of the polarization intensity of aromatic MA3 protons on GA concentration.

Comparing Figs. 9a and 7A a relationship between the polarization intensity of aromatic MA3 protons and a molar fraction of GA molecules in the micellar state can be found. Actually, the solubilization of MA3 in a micelle leads to a substantial change of its nearest environment. As compared with the hydrophilic environment in a homogeneous solution, in the micelle, the MA3 molecule is in the hydrophobic environment which, in turn, favors the reduction of the intramolecular hydrogen bond. In our opinion, this is the cause of the change in the polarization intensity with varying GA concentration. To verify another possible ways of the action of GA on MA3 photolysis which leads to a change in the acidity of a medium, the photolysis of MA3 in the same experimental conditions but in the presence of acetic acid of a similar pK value was performed. Figure 9b shows the MA3 polarization intensity versus concentration of the added acetic acid. A comparison between Figs. 9a and 9b demonstrates that the observed change in the polarization intensity upon MA3 photolysis caused by GA concentration cannot be assigned to the increase in the acidity of a medium. This also confirms the assumption of the influence of GA micelle-formation on the reactivity of solubilized compounds.

The present study demonstrates that combination of different experimental methods gives some achievements in supramolecular chemistry. By NMR (including relaxation measurements) the micellization and solubilization (or inclusion) phenomena can be detected and CIDNP method allows detect their influence on chemical reactivity of molecules solubilized in micelles (or included in host molecules) comparing to homogeneous solution. Thus, the GA micelle-formation in water-alcohol solutions was observed with cmc about 0.5–1 mM. For MA3 photolysis the dependence of reactivity both on different homogeneous solvent composition and on solubilization in GA micelles due to the equilibrium shift between intra- and intermolecular hydrogen bonding was found.

Acknowledgements We gratefully acknowledge the support of the Russian Foundation for Basic research (grant 03-03-32403).

References

1. Ploeger, B.A., Mensinga, T., et al.: The pharmacokinetics of glycyrrhizic acid evaluated by physiologically based pharmacokinetic modeling. Drug Metab. Rev. **33**, 125–147 (2001).
2. European Commission; Health and Consumer Protection; Scientific Committee on Food: Opinion of the Scientific Committee

on Food on Glycyrrhizinic Acid and its Ammonium Salt (SCF/CS/ADD/EDUL/225, Brussel, 10 April 2003).
3. Marsh, C.A., Levvy, G.A.: Glucuronide metabolism in plants. 3. Triterpene glucuronides. J. Biochem. **63**, 9–14 (1955).
4. Groen, J., Pelser, H., et al.: Effect Of Glycyrrhizinic Acid On The Electrolyte Metabolism In Addison's Disease. J. Clin. Invest. **31**, 87–91 (1952).
5. Tolstikov, G.A., Baltina, L.A., et al.: Glycyrrhizinic Acid (Review). Russian J. Bioorg. Chem. **23**, 691–709 (1997).
6. Tolstikov, G.A., Baltina, L.A., Serduyk, N.G.: Glycyrrhizinic Acid. A Review. J. Pharm. Chem. **32**, 5–14 (1998).
7. Romanko, T.V., Murinov, Yu.I.: Some peculiarities of flow of diluted Glycyrrhizinic Acid. Zhurnal. Phyzicheskoy Khimii (Physical Chemistry Journal). **75**, 1601–1904 (2001) (in Russian).
8. Tolstikov, G.A., Murinov, Yu.I., et al.: Complexes of β - Glycyrrhizinic Acid with Prostaglandins. A Novel Group of Uterotonically Active Compounds. Khimico Pharmatsevticheski Zhurnal (Chemical Pharmacetical Journal). **25**, 42–44 (1991) (in Russian).
9. Martin Del Valle E.M.: Cyclodextrins and their uses: a review. Process Biochem. **39**, 1033–1046 (2004).
10. Polyakov, N.E., Khan, V.K., et al.: Mechanisms of photoinduced electron transfer reactions of lappaconitine with aromatic amino acids. Time-resolved CIDNP study. Org. Biomol. Chem. **3**, 881–885 (2005).
11. Polyakov, N.E., Khan, V.K., et al.: Complexation of Lappaconitine with Glycyrrhizic Acid: Stability and Reactivity Studies. J. Phys. Chem. B. **109**, 24526–24530 (2005).
12. Salikhov, K.M., Molin, Yu.N., Sagdeev, R.Z., Buchachenko, A.L.: Spin Polarization and Magnetic Effects in Radical Reactions. Akamemiai Kiado, Budapest (1984).
13. Tarasov, V.F., Bagryanskaya, E.G., et al.: Examination of the exchange interaction through micellar size. 3. Stimulated nuclear polarization and time resolved electron spin resonance spectra from the photolysis of methyl deoxybenzoin in alkyl sulfate micelles of different sizes. J. Am. Chem. Soc. **117**, 110–118 (1995).
14. Parnachev, A.P., Bagryanskaya, E.G., et al.: Investigation of chemical and spin dynamic in miccelized radical pairs by time-resolved stimulated nucler polarization. Theory and experiment. Chem. Phys. Lett. **244**, 245–251 (1995).
15. Petrova, S.S., Kruppa, A.I., Leshina, T.V.: Photochemical Intracomplex Reaction between ß Cyclodextrin and Anthraquinone-2,6-disulfonic Acid Disodium Salt in Water Solution. Chem. Phys. Lett. **407**, 260–265 (2005).
16. Closs, G.L., Miller, R.J.: Laser flash photolysis with NMR detection. Submicrosecond time-resolved CIDNP: kinetics of triplet states and biradicals. J. Am. Chem. Soc. **103**, 3586–3588 (1981).
17. Goez, M.: Pseudo steady-state photo-CIDNP measurements. Chem. Phys. Lett. **188**, 451–456 (1992).
18. Carr-Purcell-Meiboom-Gill pulse sequence was used from Avance version of Bruker pulse sequence library.
19. Shimada, H., Nakamura, A., Yoshihara, T., Tobita, S.: Intramolecular and intermolecular hydrogen-bonding effects on photophysical properties of 2'- aminoacetophenone and its derivatives in solution. Photochem. Photobiol. Sci. **4**, 367–375 (2005).
20. Landolt-Börnstein: Magnetic Properties of Free Radicals, New series, **9b**, Part b (1977).
21. Landolt-Börnstein: Magnetic Properties of Free Radicals. New series, **9**, Part c1 (1979).
22. Kaptein, R.: Simple rules for chemically induced dynamic nuclear polarization. J. Chem. Soc. Chem. Commun. 732–733 (1971).
23. Emsley, J.W., Freeney, J., Sutcliffe, L.H.: High Resolution Nuclear Magnetic Resonance Spectroscopy, vol. 1. Pergamon Press, Oxford, (1965).
24. Mao, S.Z., Zhang, X.D., et al.: Nuclear magnetic resonance relaxation studies of polyacrylamide solution Colloid. Polym. Sci. **278**, 264–269 (2000).
25. Popova, M.V., Tchernyshev, Y.S., Michel, D.: NMR Investigation of the Short-chainIonic Surfactant-Water Systems. Langmuir **20**, 632–636 (2004).
26. Moroi, Y.: Micelles. Theoretical and Applied Aspects. Plenum Press, New York, (1992).
27. Jönsson, B., Lindman, B., Holmberg, K., Kronberg, B.: Surfactants and Polymers in Aqueous Solution. Wiley, Chichester (1998).
28. Jones, M.N., Chapman, D.: Micelles, Monolayers, and Biomembranes. Wiley, New York (1995).