Optics and Spectroscopy, 2025, Vol. 133, No. 4

02

Dynamics of ion solvation in binary solvent acrylonitrile/dimethyl sulfoxide

© *K.Sh. Rabadanov*[1,2], *M.A. Akhmedov*[1,2], *A.G. Magomedova*[1]

[1] Dagestan State University, Makhachkala, Dagestan Republic, Russia
[2] Dagestan Federal Research Center, Russian Academy of Sciences, Makhachkala, Dagestan Republic, Russia
e-mail: rksh83@mail.ru

Received October 29, 2024
Revised February 28, 2025
Accepted March 04, 2025

Raman spectra of solutions of lithium and sodium trifluoromethanesulfonates in the binary solvent acrylonitrile (AN)-dimethylsulfoxide have been considered. It was found that in the $Li^+(AN)_x$ and $Na^+(AN)_x$ solvatocomplexes the modulation times of the CN bond vibrations of acrylonitrile molecules (τ_ω) are much larger than those for unbound acrylonitrile. Such a ratio between τ_ω for bound and free molecules can be considered as a dynamic criterion for ion solvation in acrylonitrile solutions.

Keywords: Solvation, mixed solvent, vibrational dephasing.

DOI: 10.61011/EOS.2025.04.61409.7275-24

Introduction

The problem of cation solvation in solutions is of great fundamental and applied research interest [1–3]. Vibrational spectroscopy provides ample opportunities in the study of solvation; specifically, it allows one to determine the composition and evaluate the stability constants of solvatocomplexes [4–6]. Spectroscopy also makes it possible to examine the interactions of cations with a solvent at the molecular level and identify characteristic vibrations that serve as indicators of specific types of interactions, such as hydrogen bonds and ion–dipole and ion–ion interactions.

In addition, vibrational spectroscopy methods provide an opportunity to characterize the dynamics of particles forming a solvatocomplex within picosecond time intervals [7–9], which is an important complement to thermodynamic data.

Perelygin and Krauze have demonstrated that when lithium salts are dissolved in pyridine and acetone, the shape of Raman lines corresponding to solvent molecules becomes closer to the Lorentzian one [10,11]. A similar phenomenon was observed for solutions of lithium perchlorate in dimethyl sulfone [10]. The accompanying reduction of τ_ω, τ_V and increase in M_2 were attributed to the lack of specific solvation of lithium ions in the indicated solvents [10]. Vibrational spectroscopy has yet to provide evidence of the formation of stable solvatocomplexes in which the solvent molecules spend a considerable amount of time near lithium ions and τ_ω are large.

The examples discussed in the present study suggest that when lithium (LiTf) and sodium (NaTf) trifluoromethanesulfonates (triflates) are dissolved in the binary acrylonitrile (AN)-dimethyl sulfoxide (DMSO) solvent, AN molecules are bound into solvatocomplexes with Li^+ and Na^+ and the collisions of AN molecules with the immediate environment in these complexes become significantly more frequent than in the pure solvent.

Experimental methods

Solutions were prepared from lithium trifluoromethanesulfonate (Triflate, Aldrich), sodium trifluoromethanesulfonate (Aldrich, 99.995%), dimethyl sulfoxide (Aldrich, anhydrous, 99.8%, $< 0,005\,\%$ water), and acrylonitrile (Aldrich, $> 99\,\%$). The initial products were used as purchased.

A Senterra confocal Raman microscope (Bruker, Germany) was used to examine the Raman spectra of salt systems. The spectrum measurement parameters were as follows: excitation laser wavelength — 532 nm, laser power — 20 mW, aperture — $50 \times 1000\,\mu$m slit, spectral range — $50 - 3700\,cm^{-1}$ with a resolution of $3 - 5\,cm^{-1}$, microscope objective — 20×, number of scans — 20, and integration time of each scan — 20 s. The standard OPUS 6.0 package was used to separate complex profiles of vibrational bands into individual components. The shape of bands was approximated by curves in the form of a convolution of Gaussian and Lorentzian functions. The calculated curves were fitted to the initial spectrum using the Levenberg–Marquardt method with absolute error minimization. The mismatch between the calculated and actual curves was $5 - 10\,\%$ (depending on the signal-to-noise ratio of the original spectrum). All spectra were recorded at room temperature.

Results and discussion

It was demonstrated in [11] through the analysis of integrated line intensities that cations have a maximum

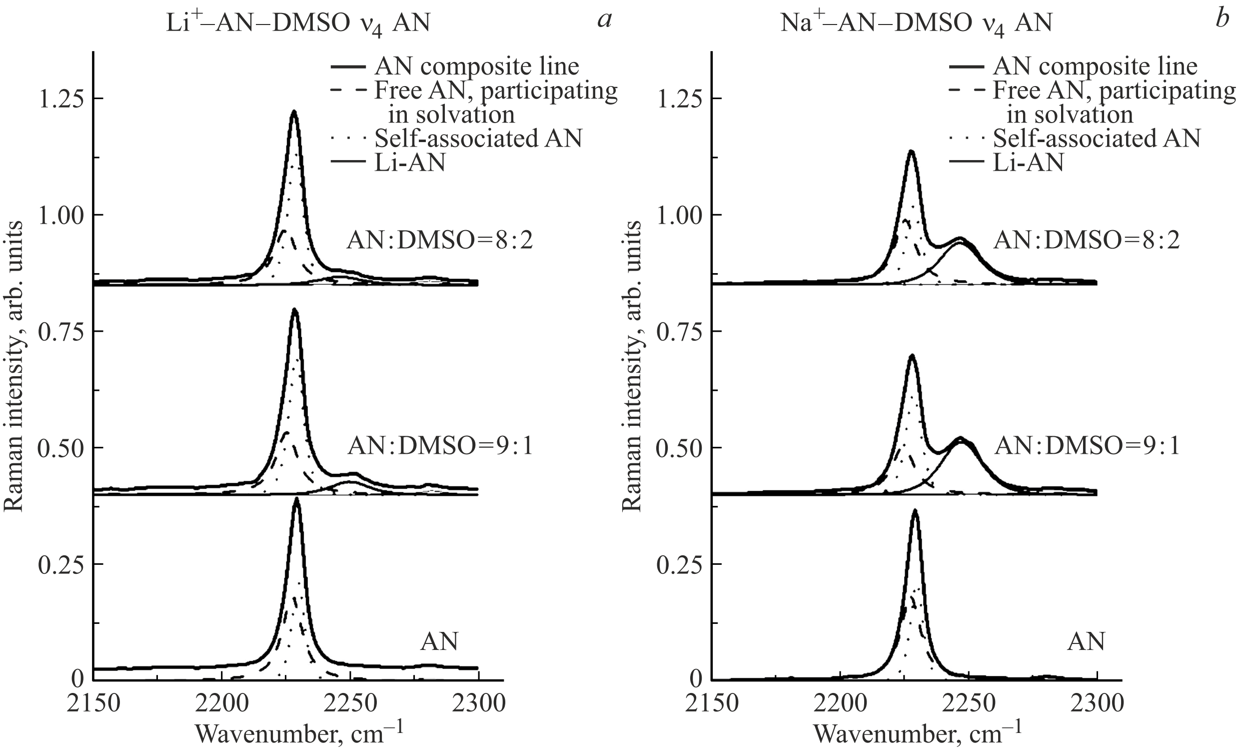

Figure 1. Raman spectra of vibration ν_4 of the C-N bond of acrylonitrile in lithium (a) and sodium (b) triflate solutions in binary system AN-DMSO.

coordination number of 4 in a mixed solvent and the number of solvent molecules surrounding the cations depends on the AN-DMSO ratio. Sodium cations do not reveal a trend toward preferential coordination of molecules of a certain solvent, whereas the solvation of lithium cations by dimethyl sulfoxide molecules appears to be preferential.

The acrylonitrile line at 2228 cm^{-1}, which corresponds to stretching vibration $\nu_4(A')$ (the one most sensitive to coordination by cations) of the C-N bond [11–15], was chosen for analysis. Degree of depolarization ρ of this line under cylindrical excitation is 0.3 [16]. This is lower than the value of 0.2 typical of the common ninety-degree excitation arrangement; i.e., the differences between the unpolarized and isotropic Raman spectra may be neglected in the first approximation.

One of the methods for studying the dynamics of molecules in a liquid is the analysis of time correlation functions (TCFs) $G(t)$ derived via Fourier transform of isotropic Raman spectra $I(\nu)$ [17–23]:

$$G(t)=\int_{-\infty}^{+\infty} I(\nu)\exp(2\pi i c\nu t)d\nu, \qquad (1)$$

where c is the speed of light. It is widely believed that the main reason for broadening of the isotropic Raman line is vibrational dephasing. In the case of vibrational dephasing, the interaction of a particle with its environment (perturbation) leads to time-dependent changes (modulation) of vibrational frequency $\Delta\omega = f(t)$ and to a vibration phase fault. If the vibrational frequency varies exponentially with time ($G_\omega(t)=\exp(-t/\tau_\omega)$, where τ_ω is the modulation time), the TCF of vibrational dephasing is characterized [19] by the Kubo equation:

$$-\ln G(t)/M_2\tau_\omega^2 = \exp(-t/\tau_\omega) - 1 + 1/\tau_\omega, \qquad (2)$$

where $M_2=\int \nu^2 I(\nu)d\nu/\int I(\nu)d\nu$ is the second moment of the vibrational spectrum (perturbation dispersion). The TCF and the spectrum vary with perturbation time: at $\tau_\omega \to 0$ (the particle environment is mobile, perturbations are weak, and interactions are non-specific), the dephasing TCFs are exponential and the spectra have a Lorentzian shape; at $\tau_\omega \to \infty$ (perturbations are strong, specific, and directed and the molecule and its environment form a rigid quasi-lattice), the dephasing TCFs and the spectra become Gaussian. Another process parameter is dephasing time τ_V, which is defined as the integral of $G(t)$:

$$\tau_V=\int G(t)dt.$$

Two components were revealed by analyzing the profile of the acrylonitrile line at 2228 cm^{-1} in the AN-DMSO system. One of them (the one positioned at lower wave numbers) has a near-Lorentzian shape (Fig. 1, dashed curve), and the other is positioned at higher wave numbers and is near-Gaussian in shape (Fig. 1, dotted curve). Their dephasing parameters differ significantly (see the table).

Solvation numbers, spectroscopic characteristics, and dephasing parameters for the NaTf-AN-DMSO and LiTf-AN-DMSO systems

Parameter	AN	AN:DMSO=9:1	AN:DMSO=8:2	AN:DMSO=9:1	AN:DMSO=8:2	AN:DMSO=9:1	AN:DMSO=8:2
				$c_{Na^+} \sim 1.44\,\mathrm{mol{\cdot}L^{-1}}$		$c_{Li^+} \sim 1.32\,\mathrm{mol{\cdot}L^{-1}}$	
$\bar{n}_{\mathrm{AN}}$				2.53	2.07	0.93	0.48
$\bar{n}_{\mathrm{DMSO}}$				0.80	1.66	1.00	2.01
„Free“ solvent							
ν, cm^{-1}	2227.5	2226.2	2225.7	2224.6	2224.4	2225.3	2224.8
M_2, ps^{-2}	21.4	25.3	24.3	19.9	15.72	21.9	20.8
τ_V, ps	1.2	1.1	1.1	1.1	1.1	1.1	1.1
τ_ω, ps	0.042	0.036	0.037	0.049	0.059	0.044	0.046
I_{int}, arb. units	2.6	3.8	3.4	1.6	1.5	2.0	1.9
Hydrogen-bonded solvent							
ν, cm^{-1}	2229.8	2228.96	2228.6	2228.6	2228.3	2229.0	2228.7
M_2, ps^{-2}	0.42	0.42	0.46	0.66	0.69	0.68	0.58
τ_V, ps	2.5	2.5	2.4	2.0	1.9	2.1	2.1
τ_ω, ps	1.9	1.96	1.9	1.5	1.4	1.2	1.7
I_{int}, arb. units	1.4	1.7	1.65	1.82	1.8	2.4	2.3
Solvent bound into a solvatocomplex							
ν, cm^{-1}				2247.2	2246.5	2249.8	2246.1
M_2, ps^{-2}				3.72	3.71	3.88	3.72
τ_V, ps				0.77	0.76	0.80	0.73
τ_ω, ps				0.93	0.99	0.69	1.32
I_{int}, arb. units.				2.4	2.0	0.6	0.4

Since τ_ω for the first line is much smaller than for the second one, one may conclude that the line at lower wave numbers corresponds to free AN molecules, while the line at higher wave numbers corresponds to hydrogen-bonded $(\mathrm{AN})_x$ associates [24]. It is clear that the line profile changes little when DMSO is added to pure acrylonitrile, which is confirmed by the similarity of dephasing parameter values (see the table).

It was noted in spectroscopic studies of acetonitrile that the line in the region of stretching vibrations of the C-N bond could be the envelope of the fundamental tone and the hot band [25]. If this were true for acrylonitrile, the broadening mechanism for the $1 \rightarrow 0$ and $2 \rightarrow 1$ transitions should be the same, the modulation time should be the same, and the line shape should be identical. Since this contradicts the calculated data (see the table), the assumption regarding the presence of a hot band in the spectra of acrylonitrile is not confirmed.

When lithium or sodium salts are added to the AN-DMSO system, a new component appears in the region of stretching vibrations $\nu_4(A')$ of the C-N bond at large wave numbers ($2247\,\mathrm{cm}^{-1}$). It corresponds to the vibrations of acrylonitrile molecules solvating Li^+ and Na^+ cations. A redistribution of intensities of the acrylonitrile line components is also observed. Analyzing the observed changes in intensity, one finds that free AN is consumed during solvation (the intensity decreases), while the amount of associated AN remains unchanged. This is quite logical, since the involvement of free acrylonitrile molecules in the formation of solvates is thermodynamically more favorable than the destruction of associates. According to the results of measurements carried out in [11], the average coordination number (solvation number) of lithium ions does not exceed unity. Intriguingly, the solvating capacity of dimethyl sulfoxide is much greater than that of acrylonitrile. The solvation numbers for dimethyl sulfoxide in the AN-DMSO system are 3.5–4 [11]. Figure 2 shows the time correlation functions for the systems under study, and their parameters are listed in the table. It turns out that the τ_ω values for vibrations of acrylonitrile molecules solvating Li^+ and Na^+

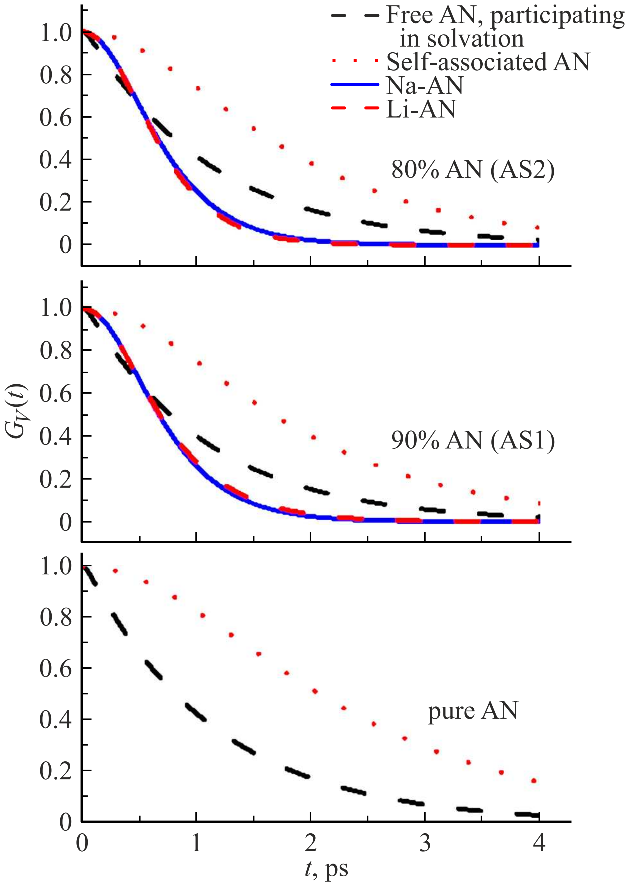

Figure 2. Time correlation functions of dephasing of vibration ν_4 of the C-N acrylonitrile bond in lithium and sodium triflate solutions in the AN-DMSO binary system.

cations are much higher than the corresponding values for vibrations of unbound acrylonitrile. Thus, cation solvation may be regarded as a directed interaction of cations with a nitrogen atom of the C-N bond of an acrylonitrile molecule. Such a relation between the τ_ω values for bound and free molecules provides a dynamic criterion for ion solvation in acrylonitrile solutions.

Conclusions

A new approach to assessing the solvation of lithium and sodium ions in the binary acrylonitrile-dimethyl sulfoxide solvent based on the analysis of modulation time τ_ω of the CN-bond vibrations of acrylonitrile molecules was presented. The obtained data demonstrate that the modulation time may serve as a dynamic criterion for quantitative assessment of the stability and directionality of solvatocomplexes. This method may be used efficiently in the study of non-aqueous electrolytes to improve the performance of batteries and other electrochemical devices. The reported results lay the foundation for further research aimed at applying this criterion in various systems.

Funding

This study was supported by the Russian Science Foundation, grant № 23-23-00247, https://rscf.ru/project/23-23-00247

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] J. Xing, S. Bliznakov, L. Bonville et al. Electrochem. Energy Rev., **5**, 14 (2022). DOI: 10.1007/s41918-022-00131-z
[2] K. Xu. Chem. Rev., **104** (10), 4303 (2004). DOI: 10.1021/cr030203g
[3] E. Quartarone, P. Mustarelli. J. Electrochem. Soc., **167**, 050508 (2020). DOI: 10.1149/1945-7111/ab63c4
[4] I.S. Perelygin. In: *Ionic Solvation*, ed. by G.A. Krestov (Ellis Horwood, Chichester, 1994). P. 100.
[5] J.M. Alía. In: *Handbook of Raman Spectroscopy*, eds. I.R. Lewis, H.G.M. Edwards (Mar-cel Dekker, N.Y., 2001). P. 617.
[6] W. Henderson, M.L. Helm, D.M. Seo, P. Trulove, H.D. De Long, O. Borodin. J. Electro-chem. Soc., **169**, 060501 (2022). DOI: 10.1149/1945-7111/ac71d4
[7] S. Hervø-Hansen, J. Heyda, M. Lund, N. Matubayasi. Phys. Chem. Chem. Phys., **24** (5), 3238 (2022). DOI: 10.1039/d1cp04129k
[8] I.S. Perelygin, A.S. Krauze. Chem. Phys. (Russ. Ed.), **7** (9), 1231 (1988).
[9] I.S. Perelygin, A.S. Krauze. Chem. Phys. (Russ. Ed.), **8** (8), 1043 (1989).
[10] D.O. Tretyakov, V.D. Prisiazhnnyi, M.M. Gafurov, K.Sh. Rabadanov, S.A. Kirillov. J. Chem. Eng. Data, **55** (5), 1958 (2010). DOI: 10.1021/je9010123
[11] J.M. Alía, H.G.M. Edwards, E.E. Lawson. Vib. Spectrosc., **34** (2), 187 (2004). DOI: 10.1016/j.vibspec.2003.09.001
[12] Y. Hamada. J. Univ. Air, **10**, 133 (1992).
[13] M.Yu. Skripkin, P. Lindqvist-Reis, A. Abbasi, J. Mink, I. Persson, M. Sandstrom. RSC Dalton Trans., **2004** (23), 4038 (2004). DOI: 10.1039/B413486A
[14] R. Semino, G. Zaldívar, E. Calvo, D. Laria. J. Chem. Phys., **141** (21), 214509 (2014). DOI: 10.1063/1.4902837
[15] P. Kannan, N. Karthick, A. Mahendraprabu, R. Shanmugam, A. Elangovan, G. Ariva-zhagan. J. Mol. Struct., **1139**, 196 (2017). DOI: 10.1016/j.molstruc.2017.03.036
[16] F. Halverson, R.F. Stamm, J.J. Whalen. J. Chem. Phys., **16** (8), 808 (1948). DOI: 10.1063/1.1747000
[17] W.G. Rothschild. *Dynamics of Molecular Liquids* (Wiley, N.Y., 1984). 413 p.
[18] C.H. Wang. *Spectroscopy of Condensed Media. Dynamics of Molecular Interactions* (Academic, Orlando, 1985). 352 p.
[19] D.W. Oxtoby. *Adv. Chem. Phys.*, **40**, 1 (1979). DOI: 10.1002/9780470142561.ch1
[20] R.A. Kubo. In: *Scottish Universities' Summer School 1961* (Oliver and Boyd, Edinburgh, 1962). P. 23.
[21] M.M. Gafurov, K.Sh. Rabadanov. Spectrochim. Acta A, **22**, 124840 (2024). DOI: 10.1016/j.saa.2024.124840

[22] M.M. Gafurov, K.Sh. Rabadanov, M.B. Ataev, S.Sh. Makhmudov. Opt. Spectrosc., **128** (11), 1778 (2020). DOI: 10.21883/OS.2020.11.50167.111-20.

[23] S.A. Kirillov. Pure Appl. Chem., **76** (1), 171 (2004). DOI: 10.1351/pac200476010171

[24] J.M. Alía, H.G.M. Edwards, W.R. Fawcett, T.G. Smagala. J. Phys. Chem., **111** (5), 793 (2007). DOI: 10.1021/jp0663210

[25] [O.N. Kalugin, D.A. Nerukh, S.A. Eremenko, A.V. Van'kevich, A.G. Nerukh. Russ. J. Inorg. Chem., **41**, 256 (1996).

Translated by D.Safin