

A ^{13}C NMR AND DENSITY FUNCTIONAL THEORY STUDY OF CRITICAL BEHAVIOUR OF BINARY WATER/2,6-LUTIDINE SOLUTION*

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Temperature dependences of ^{13}C NMR shifts have been measured in binary water/2,6-lutidine mixture close to the lower critical solution point at $T_{\text{CL}} = 306.0 \pm 0.5$ K. In order to evaluate hydrogen bonding and solvent effect contributions to the measured chemical shifts, ^{13}C magnetic shielding tensors of non-bonded 2,6-lutidine molecule, as well as water/2,6-lutidine H-bond complex *in vacuo* and in various solvents (acetonitrile, water) have been calculated using the density functional theory (DFT) with the modified hybrid functional of Perdew, Burke, and Ernzerhof (PBE1PBE). The solvent reaction field effect has been taken into account using the polarizable continuum model (PCM). ^{13}C NMR shifts ‘order parameters’ ($\Delta\delta = |\delta^+ - \delta^-|$) and ‘diameters’ ($\phi\delta = |(\delta^+ + \delta^-)/2 - \delta_{\text{C}}|$, where δ^+ , δ^- , and δ_{C} are the chemical shifts of coexisting phases and at the critical point respectively) have been calculated for each ^{13}C signal close to T_{CL} and processed using linear regression analysis of $\Delta\delta \sim |T - T_{\text{CL}}|$ and $\phi\delta \sim |T - T_{\text{CL}}|$ in the log–log plot. It has been shown that the critical index β can be determined most correctly using temperature dependences of the ^{13}C NMR signals of C4 and C3,5 carbons of 2,6-lutidine. An evaluation of critical index of ‘diameter’ is rather imprecise because of problems of referencing of δ_{C} . The obtained $\phi\delta$ slope from C4 data (0.65 ± 0.08) are closer to 2β than to $1 - \alpha$ value. The results are discussed in the light of DFT data and within the concept of complete scaling.

Keywords: properties of molecules and molecular ions, line and band widths, shapes and shifts, density functional theory, phase separation, critical phenomena

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1. Introduction

Water/derivatives of pyridine solutions exhibit a broad variety of phase transitions and sometimes peculiar critical behaviour, particularly in the presence of ionic subsystems. Binary mixtures of water/pyridine and water/one-methyl-substituted pyridine are completely miscible, but those of water/two-methyl-substituted pyridine and water/one-ethyl-substituted pyridine exhibit very fascinating closed-loop phase diagrams [1, 2]. On the other hand, phase separations in completely miscible water/pyridine solutions can be induced by the introduction of an ionic subsystem [3, 4]. All these phenomena are studied using

a wide range of modern experimental techniques – light scattering [3–5], small angle X-ray scattering [6], NMR spectroscopy [7–9], shear viscosity and refraction index measurements [10, 11], etc. Several extremely challenging problems have been revealed during these studies, namely appearance of microheterogeneous phases or mesoscopic (of about hundred nanometres) aggregates with very large equilibration times, non-equilibrium restructuring, criticality and crossover between the solvophobic and ionic regimes, etc.

Multinuclear (^1H , ^2H , ^{23}Na , ^{81}Br) NMR was successfully applied studying water/derivatives of pyridine systems and phenomena therein [7–9]. However analogous studies using the ^{13}C NMR are absent, and thus the capabilities of this method are still

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not well-recognized. To our knowledge, the application of ^{13}C NMR critical flow [12] is the only application of ^{13}C NMR to study critical phenomena. Although quantum chemistry calculations on these systems (water/derivatives of pyridine complexes and water clusters) are substantially advanced [13–16], detailed works on magnetic shielding properties of ^{13}C nuclei are practically not available. These data can be very useful for comparative purposes evaluating the hydrogen bonding and solvent effect contributions to the experimentally measured ^{13}C chemical shifts.

The purpose of the present work was an investigation of critical behaviour of binary water/2,6-lutidine mixture in the vicinity of the lower phase separation point using ^{13}C NMR and DFT calculations of magnetic shielding tensors of ^{13}C nuclei *in vacuo* and in various solutions.

2. Experiment

Commercially available 2,6-lutidine of high purity ($\geq 99.5\%$) from Aldrich Chemical Co was used without additional purification. The water used was freshly bidistilled. The samples were prepared by weighing (± 0.1 mg) the components.

NMR experiments were carried out on a BRUKER AVANCE^{II}/400 NMR spectrometer operating at 400 and 100 MHz for ^1H and ^{13}C respectively using 5 mm BB (broad band) probe-head. The temperature in a probe was controlled with an accuracy of ± 0.5 K. The signal of 3-(trimethylsilyl) propionic acid Na salt (TSPSA) in D_2O solution in capillary insert was used as the reference and then converted to δ -scale in respect of tetramethylsilane (TMS), taking $\delta(\text{TMS}) = 0.015$ ppm [17] and correcting its weak temperature drift (0.016 ppm/deg). The D_2O in the same capillary insert was used as a lock. The NMR spectra were processed digitally using the *Mestrec* [18] and *Microcal Origin* [19] program packages.

3. DFT calculations

The calculations of the magnetic shielding tensors of the non-bonded 2,6-lutidine molecule, as well as water/2,6-lutidine H-bond complex have been performed using the density functional theory (DFT). The applied approach was previously checked in various cases [9, 20, 21] and found to be adequate for this purpose. It produces an excellent coincidence of calculated and experimentally measured ^1H NMR shift for nuclei in very

strong H-bond systems, e. g. bridge proton in pyridine-N-oxide . . . HCl complex [20], as well as for rather ‘inert’ groups, e. g. methyl group in acetonitrile [21].

The full geometry optimization of the considered systems was performed using the hybrid functional of Perdew, Burke, and Ernzerhof (PBE1PBE) [22, 23] together with the 6-311++G(*d*, *p*) and 6-311++G(2*d*, 2*p*) basis sets. These sets provide converged NMR isotropic shielding constants and especially chemical shifts at the DFT level of theory. Gaussian 03 program [24] was used for all our calculations. The same approach was applied to calculate magnetic shielding tensors. The gauge-including atomic orbital (GIAO) approach [25] was used to ensure gauge invariance of the results. In order to take into account the solvent effect, we have applied the polarizable continuum model (PCM) [26, 27]. We note that the reaction field potential in the PCM approach includes only electrostatic solute–solvent interactions. Other contributions, i. e., steric, dispersive, and repulsive interactions, are calculated by classical algorithms, modifying the solute energy, but not its wave function. We have used default settings of the PCM as implemented in Gaussian 03.

4. Results and discussion

A binary water/2,6-lutidine mixture was chosen for investigation for the following reasons. First of all, its phase diagram and the values of critical parameters are well-known, see [8, 28] and references therein. Furthermore, the most precise ^2H NMR experiment has been carried out on D_2O /2,6-lutidine solution [8]. In that study a specially constructed NMR probe-head allowed authors to achieve the temperature stabilization accuracy within ± 0.005 K. The value of the critical index β , obtained from the split ^2H NMR signal of D_2O temperature evolution, was determined using the linear regression analysis in log–log plot:

$$\Delta\delta = |\delta^+ - \delta^-| \sim |T - T_{\text{CL}}|^\beta, \quad (1)$$

where δ^+ and δ^- are the chemical shifts of coexisting phases. The value of critical index $\beta = 0.336 \pm 0.030$ was in a perfect agreement with data found for many other systems with solvophobic criticality. Unfortunately no place for additional tube or capillary insert for external reference signal was designed in that NMR probe-head. Thus, because of no reference peak (single or doubled D_2O signal only), the criticality of the ‘diameter’ of chemical shift

$$\phi\delta = \left| \frac{\delta^+ + \delta^-}{2} - \delta_{\text{C}} \right|, \quad (2)$$

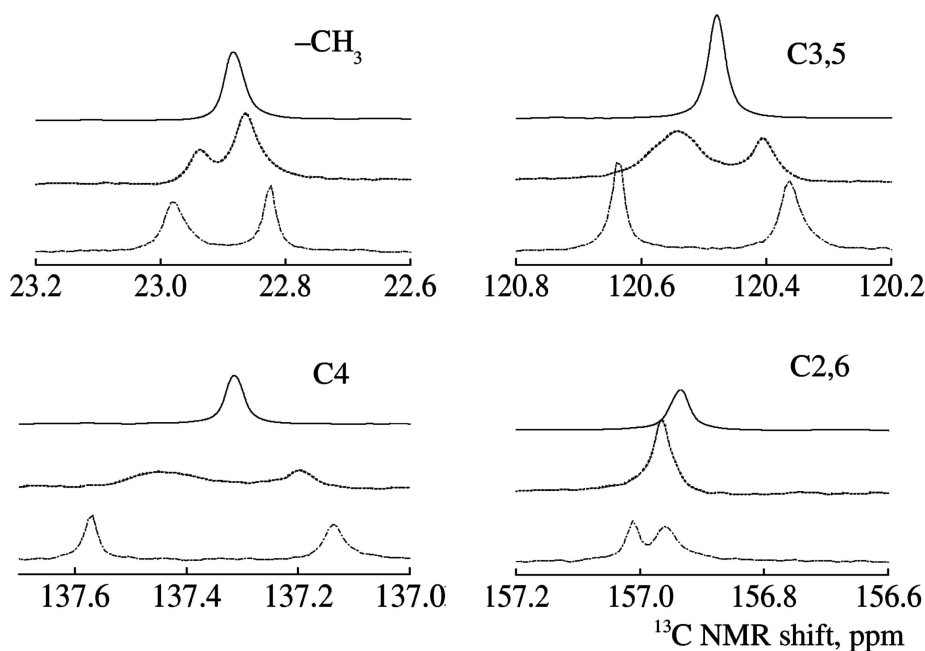


Fig. 1. Temperature evolution of ^{13}C NMR signals of different carbons of 2,6-lutidine aqueous solution (0.937 mole fraction of H_2O) in the homogenous (305 K, solid line) and phase-separated mixtures at 306 (dot line) and 316 K (dash-dot line). For carbons numbering see Fig. 3.

where δ_{C} is the chemical shift at the critical point, was not investigated.

In the present work a new experiment on $\text{H}_2\text{O}/2,6$ -lutidine system has been performed using a standard NMR probe-head that allowed temperature stabilization with an accuracy of ± 0.5 K. It enabled us to investigate the temperature behaviour for the ‘order parameter’ (1) as well as for the ‘diameter’ (2) of chemical shifts. $\text{H}_2\text{O}/2,6$ -lutidine solution of 0.937 mole fraction of H_2O , i. e. the value between those found in literature [8, 28] was prepared. The splitting of NMR signal was observed at 306.0 ± 0.5 K, and this temperature was recognized as the lower critical solution point T_{CL} .

The observed temperature evolution of ^{13}C NMR signals of different carbons of 2,6-lutidine aqueous solution crossing T_{CL} are shown in Fig. 1, and the measured temperature dependences of ^{13}C NMR shifts in the homogenous and phase-separated mixtures are presented in Fig. 2. Note, that the whole effect of phase separation on ^{13}C chemical shifts is extremely fine, e. g., the ^{13}C NMR signals are split at $T - T_{\text{CL}} = 10$ K by ~ 0.8 ppm for C4 (for numbering see Fig. 3) carbon and for C2,6 carbons by ~ 0.1 ppm (!) only (Fig. 1). It means that a very high precision in the determination of chemical shifts is desirable. Even small changes of magnetic susceptibility or temperature drift of the reference signal may dramatically distort the experimental data. Moreover, the origin of so highly different behaviours of ^{13}C NMR shifts of 2,6-lutidine carbons,

Table 1. Calculated isotropic parts of ^{13}C magnetic shielding tensors of 2,6-lutidine molecule and its H-bond complex with water in various media.

Solvent	-CH ₃	C3,5	C4	C2,6
Non-bonded 2,6-lutidine				
<i>in vacuo</i>	162.016*	65.858	47.581	24.067
	161.988	66.228	47.610	24.038
CH_3CN	162.471	64.331	45.357	23.276
	162.394	64.723	45.349	23.334
H_2O	162.482	64.275	45.278	23.262
	162.403	64.664	45.267	23.321
2,6-lutidine ... H_2O complex				
<i>in vacuo</i>	163.213	64.680	46.474	23.906
	162.936	65.010	46.541	23.999
CH_3CN	163.590	63.150	44.309	24.034
	163.413	63.557	44.288	24.200
H_2O	163.581	63.080	44.227	23.974
	163.445	63.510	44.214	24.210

* the upper values correspond to 6-311++G(*d*, *p*) basis set and the lower ones to 6-311++G(2*d*, 2*p*).

namely, different temperature slopes in the one-phase region and a very different splitting, as well as interchanges in positions of the signals that correspond to the upper and lower phases above T_{CL} (Fig. 2), is not clear.

These effects most probably arise from the different hydrogen bonding (H-bond) and solvent reaction field contributions to the measured ^{13}C chemical shifts. Therefore, trying to elucidate these observations, ^{13}C magnetic shielding tensors of non-bonded 2,6-lutidine

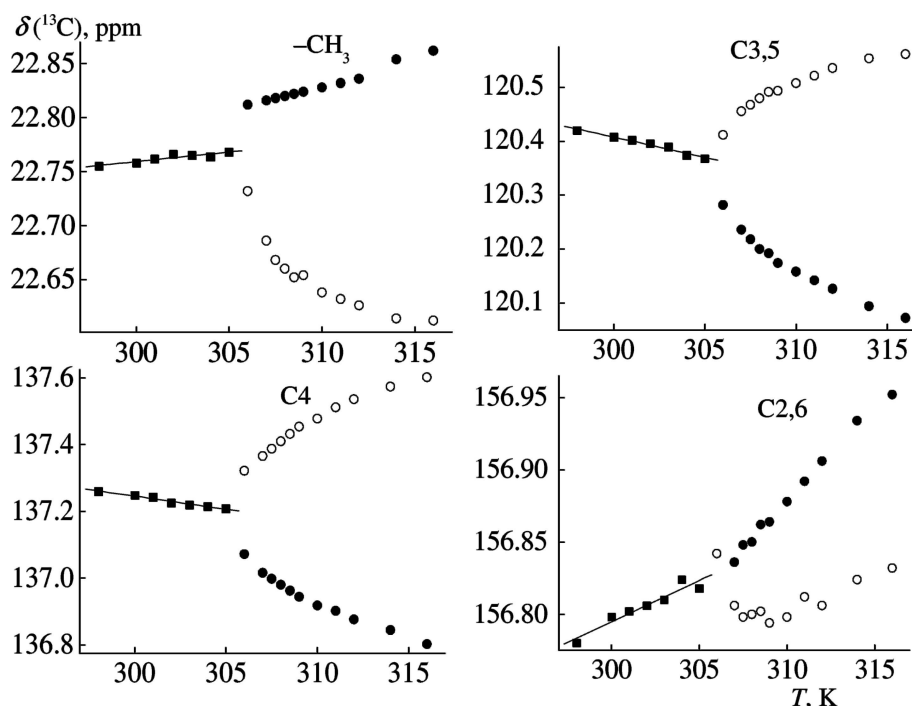


Fig. 2. Measured temperature dependences of ^{13}C NMR shifts of different carbons of 2,6-lutidine aqueous solution (0.937 mole fraction of H_2O) in the homogenous phase (below the lower critical solution point $T_{\text{CL}} = 306.0 \pm 0.5$ K) and in the phase-separated mixture – the water-rich phase (filled circles) and the 2,6-lutidine-rich phase (open circles), respectively. For carbons numbering see Fig. 3.

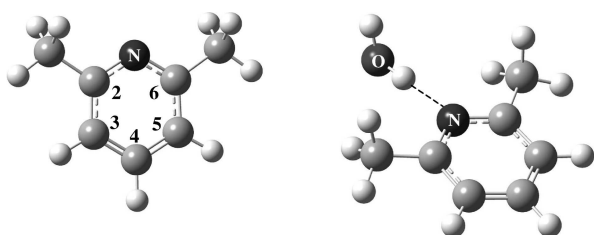


Fig. 3. Calculated structures of 2,6-lutidine and its H-bond complex with H_2O molecule.

molecule, as well as water/2,6-lutidine H-bond complex (Fig. 3) *in vacuo* and in various solvents (acetonitrile, water) have been calculated using the density functional theory (DFT). The calculated values of isotropic parts of magnetic shielding tensors ($\sigma_{\text{iso}} = 1/3 \text{Tr } \sigma$) of ^{13}C nuclei of 2,6-lutidine and its H-bond complex with water molecule in various media are collected in Table 1.

Furthermore, since it is clear that the studied effects are small, and very high precision handling chemical shifts is required, the earlier estimated values of magnetic shielding tensors of ^{13}C and ^1H nuclei of the reference molecule (TMS) [20, 21] have been revised recalculating them in various solvents using the above DFT approach. These new values are given in Table 2.

Then the ^{13}C chemical shifts of the investigated molecular structures (non-bonded 2,6-lutidine and water/2,6-lutidine H-bond complex) were transformed to

Table 2. Calculated isotropic parts of magnetic shielding tensors of ^{13}C and ^1H nuclei of the tetramethylsilane (TMS).

Basis	Solvent	$\sigma_{\text{iso}}(^{13}\text{C})$, ppm	$\sigma_{\text{iso}}(^1\text{H})$, ppm
6-311++G(d, p)	<i>in vacuo</i>	189.07	31.81
	CH_3CN	189.85	31.78
	H_2O	189.87	31.78
6-311++G(2d, 2p)	<i>in vacuo</i>	188.33	31.65
	CH_3CN	189.08	31.62
	H_2O	189.11	31.61

the δ -scale as the difference between the calculated isotropic magnetic shielding (σ_{iso}) and that of the TMS. The DFT predictions of the H-bond and solvent effect contributions to the ^{13}C chemical shifts of various 2,6-lutidine carbons are shown in Fig. 4. Since both calculations using two basis sets revealed no crucial quantitative differences, only the results obtained with 6-311++G(2d, 2p) basis set are presented in Fig. 4. It is obvious that these contributions for C4 and C3,5 indeed are much higher than those for C2,6 and $-\text{CH}_3$. This effect exactly correlates in the extent of splitting of ^{13}C NMR signals observed in the coexisting phases (Fig. 1). Moreover, the origin of different signs of the slopes of temperature dependences $\delta(^{13}\text{C}) = f(T)$ in the homogeneous phase (Fig. 2) comes clear now. As it is easy to see in Fig. 4, the formation of the H-bond complexes with water reduces the ^{13}C chemical shifts

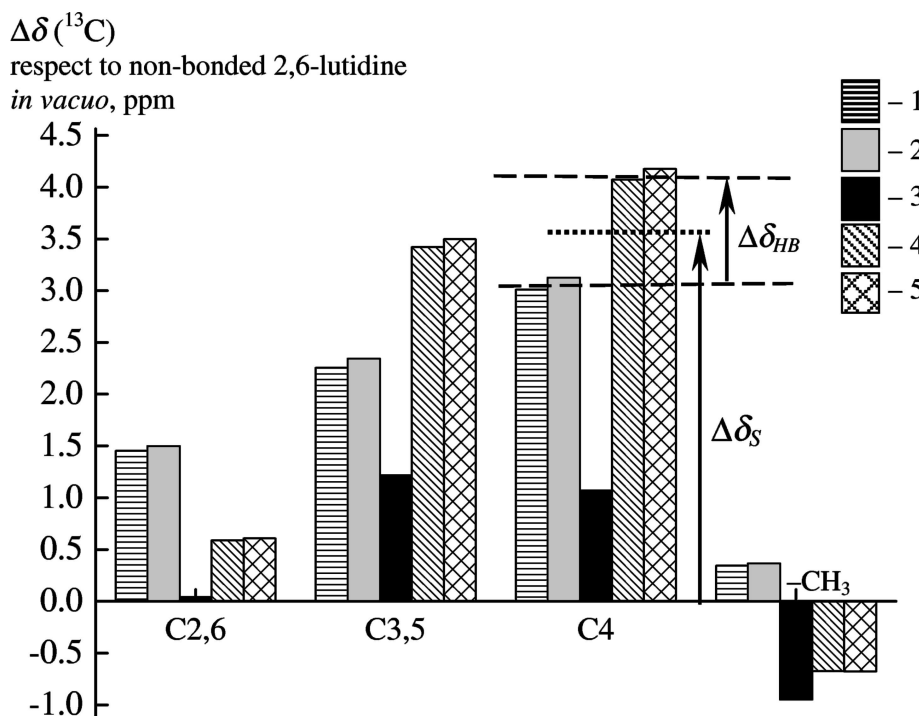


Fig. 4. Solvent effect ($\Delta\delta_S$) and H-bond ($\Delta\delta_{HB}$) contributions to the ^{13}C NMR shifts of different carbons of 2,6-lutidine molecule predicted by DFT-PCM (6-311++G(2d, 2p)): 1, 2 for non-bonded molecule in acetonitrile and H_2O respectively; 3–5 for the H-bond complexes *in vacuo*, in acetonitrile, and H_2O respectively. In order not to overload the figure, $\Delta\delta_S$ and $\Delta\delta_{HB}$ contributions are pictured for C4 only. Other comments see in text.

of C2,6 and $-\text{CH}_3$ carbons. Hence their chemical shifts have to increase with temperature in contrast to C4 and C3,5 signal behaviour. This is also observed experimentally (Fig. 2).

^{13}C NMR shift ‘order parameters’ $\Delta\delta$ (1) and ‘diameters’ $\phi\delta$ (2) have been calculated for each ^{13}C signal in 306–316 K range and processed using the linear regression analysis of $\Delta\delta \sim |T - T_{CL}|$ and $\phi\delta \sim |T - T_{CL}|$ in the log–log plot. It comes out that the critical index β can be determined most correctly using temperature dependences of the ^{13}C NMR shifts of C4 and C3,5 carbons of 2,6-lutidine, i. e. exploiting the experimental information that comes from the nuclei having the most sensitive shielding in respect of the H-bonding and media effects. Despite of a limited accuracy of temperature stabilization (± 0.5 K), the obtained values of β between 0.325 ± 0.05 (C3,5) and 0.344 ± 0.05 (C4) are very close to those estimated using ^1H and ^2H NMR data for this system [8, 9]. A processing of corresponding data for much less sensitive carbons leads to unrealistic values of this critical index, namely 0.65 (C2,6) or 0.22 ($-\text{CH}_3$).

An evaluation of the critical index for ‘diameter’ is rather imprecise because of problems with referencing of δ_C in (2). A temperature drift of the external reference signal can be fatally disastrous when processing

so fine temperature effects. In the present work it was attempted to correct this drift trying to reproduce the well-known slope $\Delta\delta/\Delta T = -0.0188$ ppm/deg in the neat water [29], i. e. for the signal of residual H_2O in $\text{D}_2\text{O}/\text{TSPSA}$ solution in the capillary insert used for lock. But of course, this can be considered only as a rather rough treatment. Therefore the ^{13}C NMR shifts of C4 and C3,5 carbons have been recalculated referencing them in respect of the signal of methyl groups of 2,6-lutidine molecules, i. e. with respect to an internal standard. It was a successful approach that led to very realistic values of critical indices. The obtained $\phi\delta$ slope for C4 data set 0.65 ± 0.08 is much closer to 2β than to $1 - \alpha$ (with $\alpha = 0.110$, [28]) value. It is suggested that the term in the ‘diameter’ of coexistence curves containing $|T - T_C|^{2\beta}$ singularity arises from a ‘wrong’ choice of composition variables [30]. However, the above result is consistent with the new concept of ‘complete scaling’ in the theory of critical phenomena formulated in [31] and examined experimentally in [32]. The term having 2β -criticality may appear to be significant, if the competition between two correlations – concentration and entropy and correlation between concentration and molar density – takes place in the mixture [32]. Our finding can be considered as an additional experimental support to this concept.

5. Concluding remarks

First of all note, that the applied DFT treatment using the PBE1PBE functional, despite being quite simple (i. e. standard functional and solvent effects by PCM), correctly predicts the sign and the scaling of H-bond and solvent effects on ^{13}C magnetic shielding properties. It means that this approach can also be applied to explain temperature dependences of ^{13}C NMR shifts in other related systems and to model the critical behaviour of ^{13}C chemical shifts close to the phase transition point. The experimental ^{13}C NMR work carried out in the present study opens the ways for a wider use of this method to study critical phenomena in aprotic, non-aqueous solutions, ionic liquids, systems with biological importance, etc, where ^1H NMR measurements are not possible or may be too complicated. And finally, the values of critical indices, obtained from ^{13}C NMR and from earlier ^1H NMR studies on this solution [9], support the concept of ‘complete scaling’.

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KRIZINĖS DVINARIO VANDENS/2,6-LUTIDINO TIRPALO ELGSENOS TYRIMAI TAIKANT ^{13}C BMR SPEKTROKOPIJĄ IR TANKIO FUNKCIONALO TEORIJĄ

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Santrauka

Pastaruoju metu dėl augančio susidomėjimo heterogeninių sistemų ir molekulių nano-spiečių formavimosi vyksmais vis svarbesniais tampa įvairių vandens darinių (vandens/organinių sandų tirpalų, sistemų su joniniais sandais ir kt.) krizinių savybių ir krizinių parametrų įvertinimai. Darbe buvo eksperimentiškai išmatuotos vandens/2,6-lutidino tirpalo ^{13}C BMR poslinkių priklausomybės nuo temperatūros žemutinio krizinio taško $T_{\text{CL}} = 306,0 \pm 0,5$ K artumoje. Siekiant įvertinti vandenilinio ryšio (H ryšio) ir terpės reakcijos lauko indėlius išmatuotiesiems cheminiams poslinkiams, pasitelkus kvantinės mechanikos tankio funkcionalo teoriją (DFT), buvo apskaičiuoti 2,6-lutidino molekulės bei vandens ir 2,6-lutidino H-ryšio kompleksų vakuume ir įvairiuose tirpikliuose (acetonitrile, vandenyje) anglies magnetinio ekranavimo tenzorai. Skaičiavimai buvo atlikti taikant modifikuotąjį hibridinį Perdew, Burke ir Ernzerhof funkcionalą (PBE1PBE) bei GIAO atominių or-

bitalių artinį. Į dielektrinės terpės reakcijos lauką atsižvelgta pritaikant poliarizuojamojo kontinuumo modelį (PCM). ^{13}C BMR cheminių poslinkių „tvarkos parametras“ $\Delta\delta = |\delta^+ - \delta^-|$ ir „skersmuo“ $\phi\delta = |(\delta^+ + \delta^-)/2 - \delta_{\text{C}}|$ (čia δ^+ , δ^- ir δ_{C} atitinkamai yra sambūvio fazių ir krizinio taško cheminiai poslinkiai) buvo apskaičiuoti visiems ^{13}C BMR signalams ir apdoroti, atliekant priklausomybių $\Delta\delta \sim |T - T_{\text{CL}}|$ ir $\phi\delta \sim |T - T_{\text{CL}}|$ tiesinę regresijos analizę dvigubuose logaritminiuose (log–log) grafikuose. Parodyta, kad tiksliausiai šios sistemos tvarkos parametro krizinis rodiklis β gali būti nustatytas remiantis 2,6-lutidino C4 ir C3,5 anglies BMR signalų priklausomybėmis nuo temperatūros. „Skersmens“ krizinę elgseną tirti yra labai sunku dėl atskaitos signalo problemų matuojant δ_{C} . Priklausomybės $\log \phi\delta \sim \log |T - T_{\text{CL}}|$ polinkis $0,65 \pm 0,08$, nustatytas remiantis C4 duomenimis, yra artimesnis 2β nei $1 - \alpha$ vertėms. Gautosios išvados pagrindžiamos DFT skaičiavimų rezultatais ir aptariamoms krizinių reiškinių pilno mastelio invariantiškumo požiūriu.