

PREFERENTIAL SOLVATION OF AMIDES BY METHANOL – A COMPARISON OF MOLECULAR DYNAMICS CALCULATIONS WITH THE EXPERIMENTAL DATA

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Abstract: Using the Kirkwood-Buff theory of solutions, the preferential solvation of the *N*-methylacetamide (NMA), *N*-methylformamide, (NMF), and *N,N*-dimethylformamide, (DMF), molecule has been investigated in the binary {amide+methanol} mixtures at 313.15 K. Moreover, for the {amide+methanol} mixtures, where amide = NMF, DMF, and NMA, the molecular dynamics calculations at $x_{amide} = 0.518$ were performed. From the obtained molecule-molecule radial distribution functions, (rdf), and atom-atom rdf, it was possible to estimate the local mole fractions around the amide molecule, the orientation effects of molecules within the solvation shell, and a possibility of the formation of complexes. The general picture obtained from analysis of the molecular dynamics results is consistent with the deductions derived from thermodynamic data.

Keywords: amides, alcohols, preferential solvation, Kirkwood-Buff integrals, molecular dynamics simulations

1. Introduction

This work continues the series of papers describing the solvation of amides in binary and ternary mixtures containing amide, water, and/or aliphatic alcohol. In the previous papers, the solvation of *N,N*-dimethylformamide [1] (DMF) and *N*-methylformamide [2] (NMF) was investigated. The conclusions, however, were derived from thermodynamic data only. In this work the molecular dynamics results for binary mixtures {amide+methanol} are reported, and comparison with the thermodynamics conclusions is made.

The amide group can serve as a model of the peptide bond, and interactions between hydroxy and amide groups play an important role in the solvation of peptides in aqueous solutions. As a result of the intermolecular interactions, a preferential solvation of molecules is observed. We understood that preferential solvation arises if the local mole fractions of solvent components in a solvational microsphere surrounding the solute differ from the bulk ones. Preferential solvation is always present and, although in some cases it is relatively weak, it affects the thermodynamic properties of solution. It is well known

that amides interact with water or alcohol as solutions by dipol-dipol interactions, and form some hydrogen-bonded complexes or heteroassociates [3–6]. The amide-water and amide-alcohol hetero-association should be different, however, on the molecular level: the water molecule creates four hydrogen bonds, while alcohol molecules may create only two hydrogen bonds, forming linear polymeric structures [7]. Thus, we can expect, that the mentioned differences will cause differences in the structure of the solvation shell. The previously obtained results [2] do not, however, confirm this expectation.

A valuable tool for investigation of the changes in the solvation microsphere is the Kirkwood-Buff theory of solutions [8]. It describes thermodynamic properties of solutions in an exact manner over the whole concentration range using quantities:

$$G_{ij} = \int_0^{\infty} (g_{ij}(r) - 1) 4\pi r^2 dr, \quad (1)$$

where $g_{ij}(r)$ is the radial distribution function. G_{ij} is called the Kirkwood-Buff integral or fluctuation integral. In other words, if radial distribution functions, g_{ij} , are known (and then the G_{ij} quantities are known too), we can determine the thermodynamic properties of solution using the equations of the Kirkwood-Buff theory [8]. On the other hand, as was pointed firstly by Ben Naim [9], the original Kirkwood-Buff theory can be inversed, and the G_{ij} parameters can be determined from experimental values of thermodynamic quantities, such as chemical potential, partial molar volumes, and isothermal compressibility factor [9]. Next, the $c_i G_{ij}$ product (where $c_i = N_i/V$ is the concentration of species i in the mixture) describes the total average excess (or deficiency) of i molecules in the entire neighbourhood of a j molecule [9–11]. Then, exploiting the idea presented previously in the literature [1, 2, 10, 11], it is possible to estimate the local mole fractions of the components of the solution; the possibility of evaluating of these quantities was pointed out by many authors [10–14] and seems a valuable and convenient tool for description of the solvation process. It should be stressed here, that the Kirkwood-Buff theory is an exact one and the determination of the G_{ij} values from thermodynamic data does not involve any assumptions. That is why the description of the solvation phenomena obtained on the basis of this approach is fully reliable, and the Kirkwood-Buff integrals formalism is a frequently applied method in investigations of solutions [15, 16].

The above considerations represent the “pure thermodynamic” point of view. The Kirkwood-Buff theory was used in the previous works [1, 2] for interpretation of the thermodynamic results. It is quite obvious, however, that the thermodynamic data can not give a detailed insight into the structure of the solvation shell. More information on the structure of the solvation microsphere around the given j molecule is contained in the radial distribution functions, g_{ij} , but these details are lost in the integration process, Equation (1). The complete information on the solution structure (the radial distribution functions, formation of complexes, or orientational effects), can be obtained from molecular dynamics (MD) calculations. We can say, the results of MD calculations may complement and confirm the conclusions obtained from the thermodynamic measurements. This is why these calculations were initiated. In this work, there are performed the calculations for the binary mixtures {amide+methanol}, where amide = NMF, DMF, and *N*-methylacetamide

(NMA) at the composition $x_{amide} = 0.518$ and results of these calculations are compared with the conclusions derived from thermodynamic data.

2. Data sources

The Kirkwood-Buff integrals and linear coefficients of preferential solvation for investigated binary mixtures were obtained from excess Gibbs energies, G^E , excess volumes of mixing, V^E , and isothermal compressibilities, κ , all at the temperature 313.15 K, were selected from the literature, mainly from previous work from this laboratory. References for {amide+methanol} systems are given in Table 1.

Table 1. References for {amide+methanol} systems

Amide	G^E	V^E
<i>N</i> -methylacetamide (NMA)	[17]	[18]
<i>N</i> -methylformamide (NMF)	[19]	[20]
<i>N,N</i> -dimethylformamide (DMF)	[21]	[22]

The isothermal compressibility factors for pure amides were taken from [23] for NMF and from [24] for DMF. Unfortunately, there are no compressibility data for NMA; this value was assumed the same as for NMF – this assumption does not influence the accuracy of the calculations [25]. On the other hand, the Monte Carlo simulations of neat liquid amides indicate [26] that compressibilities of NMA and NMF should be nearly the same. The isothermal compressibility factor for methanol was taken from [27]. Values of this factor for the investigated binary mixtures were calculated from equation:

$$\kappa = \sum_i \kappa_i \phi_i, \quad (2)$$

where κ_i is the isothermal compressibility factor of the i -th compound, and ϕ_i is its volume fraction in the mixture. Treatment of experimental data, calculations of Kirkwood-Buff integrals and linear coefficients of preferential solvation were described in detail in the previous papers [1, 2].

3. Molecular dynamics calculations

The molecular dynamics calculations were carried out by using the GROMOS 87 package [28]. Each model system consisted of 729 molecules in a cubic box with the periodic boundary conditions. The calculations were conducted at NPT ensemble, assuming a temperature of $T = 313$ K and a pressure p equal to 1 atmosphere. The molecules were represented as a collection of interacting sites: three-site for methanol and six-site model for amides. The methyl group, CH_3 , was taken as a single-site centered on the carbon atom (the united atom approximation). There are static, nonpolarizable models whose site-site interactions are sums of the Coulombic potentials and the short range Lennard-Jones term.

The energy of intermolecular interactions between the A and B molecules is given in the form:

$$E_{AB} = \sum_i \sum_j \left\{ 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}^2} \right\}, \quad (3)$$

where i represents the i -th site of molecule A , and j represents the j -th site of molecule B . The following combining rules, included in the GROMOS package, were used:

$$\sigma_{ij} = \sqrt{\sigma_i \sigma_j} \quad \text{and} \quad \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}. \quad (4)$$

The LJ potential well depth, ε_{ij} , and diameter, σ_{ij} , for the i -th site was taken from the GROMOS data base. The partial charges, q_i , were taken from [29] for methanol and from [30] for amides. The geometry parameters for amides and alcohol molecules are presented in Table 2, whereas Table 3 contains the values of the partial charges q_i at the i -th site of a molecule.

Table 2. Geometrical parameters of amide and methanol molecules. R1 and R2 symbolise the hydrogen atom or CH₃ group, linked with the C and N atoms of amide molecule, respectively

Bond lengths, nm		Bond angles, deg	
methanol			
O–H	0.1037	C–O–H	120
O–C	0.1483		
amides			
C–O	0.1272	R1–C–O	120
C–R1	0.1520 (NMA)	R1–C–N	120
	0.1035 (NMF,DMF)		
CH ₃ –N	0.1520	C–N–CH ₃	117
R2–N	0.1034 (NMA,NMF)	C–N–R2	120
	0.1520 (DMF)		
N–C	0.1375		

The initial configurations of the investigated mixtures were created by arranging the 378 NMF molecules and 351 methanol molecules in a cubic box. Then, the system was equilibrated for 200 ps approximately. Finally the 20 ps run was performed for data collection.

4. Results and discussion

4.1. Binary {amide(1)+methanol(2)} mixtures – thermodynamic results

For a description of the solvation of amides there are used the linear coefficients of preferential solvation, δ_{ij}^0 , defined as [1, 2]:

$$\delta_{ij}^0 = x_i G_{ij} - x_i \sum_k x_k G_{kj}, \quad (5)$$

where G_{ij} symbolise the Kirkwood-Buff integrals and x_i is the mole fraction of the i component. These are adequate quantities for this description, because they reflect changes

Table 3. Partial charges q_i at the i -th site of the methanol and amide molecules. R1 and R2 symbolise the hydrogen atom or CH₃ group, linked with the C and N atoms of amide molecule, respectively

Atom	q_i	Atom	q_i
methanol			
C	0.265	H	0.435
O	-0.700		
amides			
C	0.500	CH ₃	0.285 (DMF) 0.200 (NMA,NMF)
N	-0.570	R1	0.000
O	-0.500	R2	0.285 (DMF) 0.370 (NMA,NMF)

in the local mole fractions of all species around the selected central molecule. Using the δ_{ij}^0 values, the local mole fraction of the i component around the molecule of j component, x_{ij} , may be determined as:

$$x_{ij} \approx x_i + \delta_{ij}^0 / V_c, \quad (6)$$

where $V_c (= 4/3\pi R_c^3)$ is the volume of solvation shell of the radius R_c .

Figure 1 shows the δ_{21}^0 values (describing solvation of amide molecule by methanol), determined from the experimental data for all the investigated amides. As was stated previously [2, 9–11], the small absolute values of the δ_{21}^0 's (do not exceeds 20 cm³mol⁻¹) allow to conclude, that the radius of the solvation shell is small, and probably does not exceed the radius of the first coordination sphere around the amide molecule. We may define the solvation shell as a sphere of radius R_c , centered on amide molecule, and within this sphere the mole fractions of components differ from the bulk ones [10–14].

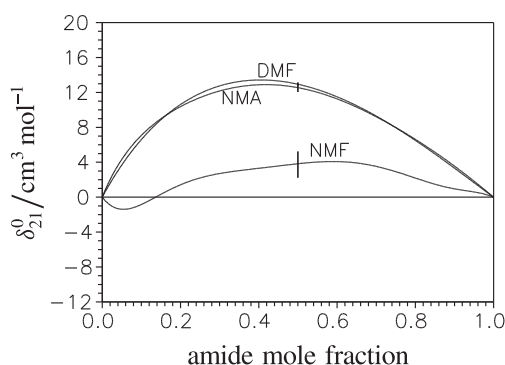


Figure 1. Concentration dependence of δ_{21}^0 values calculated from experimental data for {amide+methanol} binary mixtures. The vertical bars show the estimated error

The above conclusion can be supported by two results. First, the Marcus' investigations of binary mixtures of water and organic solvents [31] indicate, that for amides (formamide,

NMF, DMF, NMA) as organic solvents, the correlation in the second solvation (coordination) shell is very weak and disappears altogether from the third shell onwards. Second, in the case of the strongly associated solutions (for example for {alcohol+hydrocarbon} or {water+hydrocarbon} mixtures) this radius is expected large, and the δ_{ij}^0 are large exceeding $200 \text{ cm}^3 \text{ mol}^{-1}$ (or more) [32].

It can be estimated from Figure 1 and Equation (6) that for all the investigated amides the local mole fractions differ only slightly ($< 1\%$) from the bulk ones. In other words, they are nearly the same as for an ideal solution. Thus, we can conclude, that in spite of the possible interactions between amide and alcohol molecules, the distribution of molecules in the solution structure is practically completely random. The only arrangement in the solution is the one resulting from orientational effects. We can say that amide molecules “build in” into existing polymeric structure of alcohol. This indicates, that some complexes between amide and methanol molecules are formed. Formation of such associates was reported previously in the literature [3–6]. We will not discuss this in more details.

4.2. Molecular dynamics calculations

Among the investigated amides two, that is NMA and NMF, can exist in two forms: the *cis* and *trans* conformers – see Figure 2. The *trans*-to-*cis* and *cis*-to-*trans* energy barrier heights for these amides are 22.6 and 19.8 kcal/mol, respectively [33], determined from NMR measurements, and using 1,2-dichloroethane and water as solvents. Easy to calculate, the *trans* conformer is by 2.8 kcal/mol more stable. The error of these measurements is estimated to be 1.8 kcal/mol [33], and, therefore, it is not a possible evaluation of the solvent effect on the relative stability of both conformers. On the other hand, we can expect that these conformers may be different in their ability for hydrogen bond formation. Dixon *et al.* [34] have found that for NMA, the *cis* isomer is predicted to be 2.3 kcal/mol less stable than the *trans* one for the uncomplexed NMA. In the water solution, the *cis*-NMA·H₂O complex is only 0.5 kcal/mol less stable than the *trans*-NMA·H₂O complex. Taking into investigation the dimeric molecule, (NMA)₂, formed by two amide molecules, they found that *cis* isomer forms dimeric complex which is by 6.7 kcal/mol more stable than the one formed by the *trans* one. This indicates, that both, *cis* and *trans* conformers, interact with water or other amide molecules in a different manner. We can expect that in the alcohol solution, a similar behaviour should be observed. Then, for the {NMF+MeOH} and {NMA+MeOH} mixtures, the calculations for both, the *cis* and *trans* isomers, were performed separately.

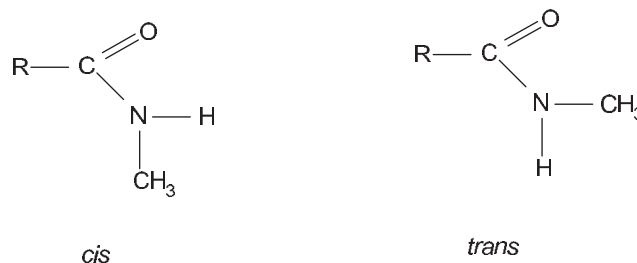


Figure 2. The *cis* and *trans* conformers of NMA and NMF molecules

The molecule-molecule radial distribution functions (rdf) $g_{11}(r)$ and $g_{12}(r)$, are shown in Figure 3, for all the investigated amides. As can be seen from this figure, a well-defined

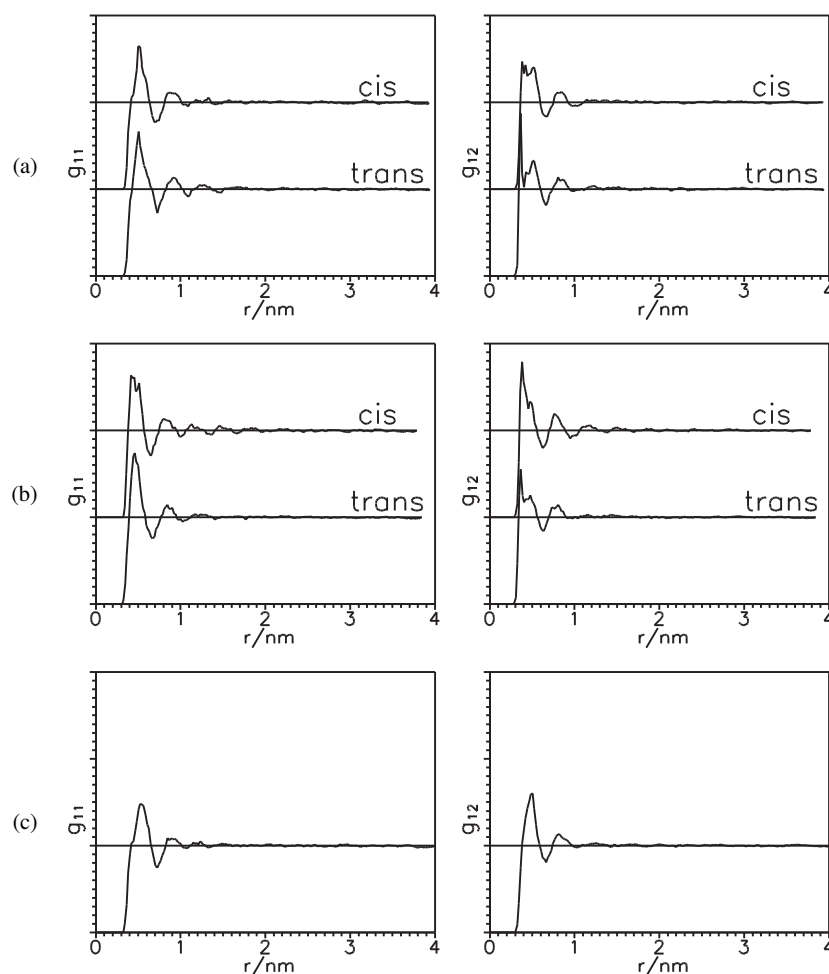


Figure 3. Molecule-molecule radial distribution functions $g_{11}(r)$ and $g_{12}(r)$ calculated for {amide(1)+methanol(2)} binary mixtures. From top to bottom: (a) amide = *N*-methylacetamide, (b) amide = *N*-methylformamide, (c) amide = *N,N*-dimethylformamide

first peak on the rdf is observed; this peak corresponds to the first coordination sphere around the amide molecule. The radius of this sphere can be estimated from the position of the first minimum of the rdf. This radius is equal to approximately 0.65 nm, and it roughly does not depend on the amide kind. Moreover, the second peak of the rdf is clearly visible too, and it corresponds to the second coordination sphere. Additionally, it can be concluded that the molecule-molecule rdf's for both, the *cis* and *trans* conformers, differ only slightly.

We define here the solvation shell as a sphere of a radius R_c , centered on amide molecule, and within this sphere the mole fractions of components differ from the bulk ones [10–14]. As was deduced from thermodynamic results above, the local mole fractions are nearly the same as for the bulk ones, and the radius of the solvation shell does not exceed the radius of the first coordination sphere. This deduction can be examined by using the MD results as follows.

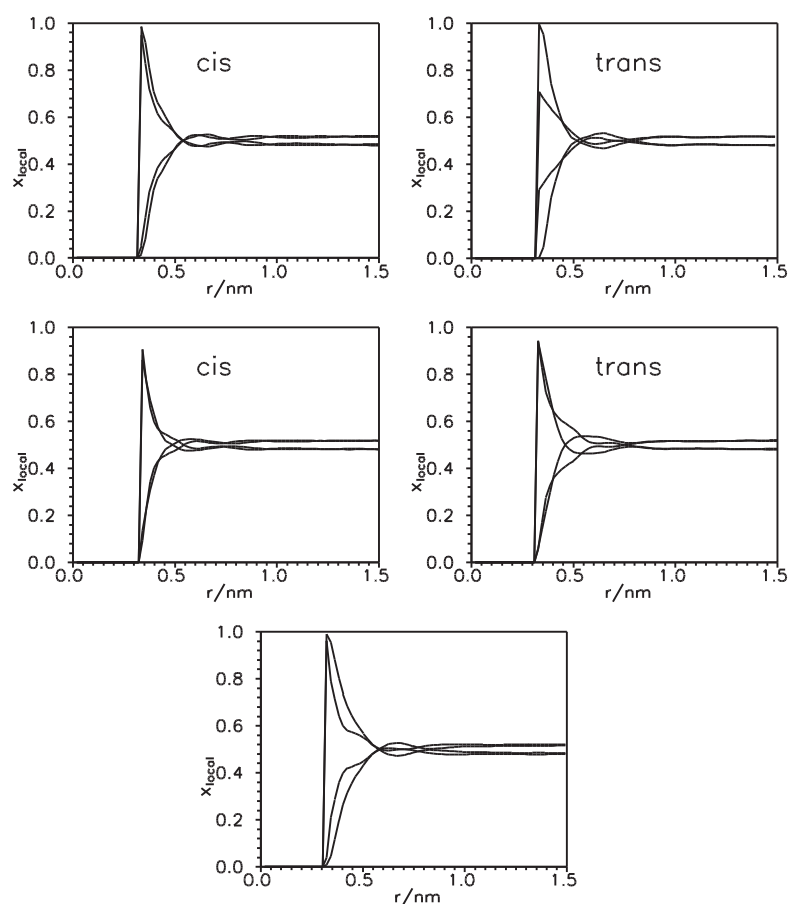


Figure 4. Values of the local mole fractions as a function of radius r , calculated from Equation (8). The graphs from top to bottom represent the NMA, NMF, and DMF results, respectively

According to the definition of the molecular radial distribution function, $g_{ij}(r)$:

$$n_{ij}(r) = \rho_i \int_0^r g_{ij}(x) \cdot 4\pi x^2 dx, \quad (7)$$

where $n_{ij}(r)$ symbolizes the number of i molecules within the sphere of radius r around the central j molecule; and ρ_i is the number density of i molecules. The local mole fractions within this sphere can be calculated as follows:

$$x_{ij}^{loc}(r) = \frac{n_{ij}(r)}{\sum_k n_{kj}(r)}. \quad (8)$$

All the $x_{ij}^{loc}(r)$ functions, calculated from this equation, are displayed in Figure 4. As can be seen, the local mole fractions at $r = 0.65$ nm (at the limit of the first coordination sphere) nearly do not differ from the bulk ones. This means, that the radius of the solvation shell does not exceed the value $R_c = 0.65$ nm, which confirms the previous “thermodynamic” deductions.

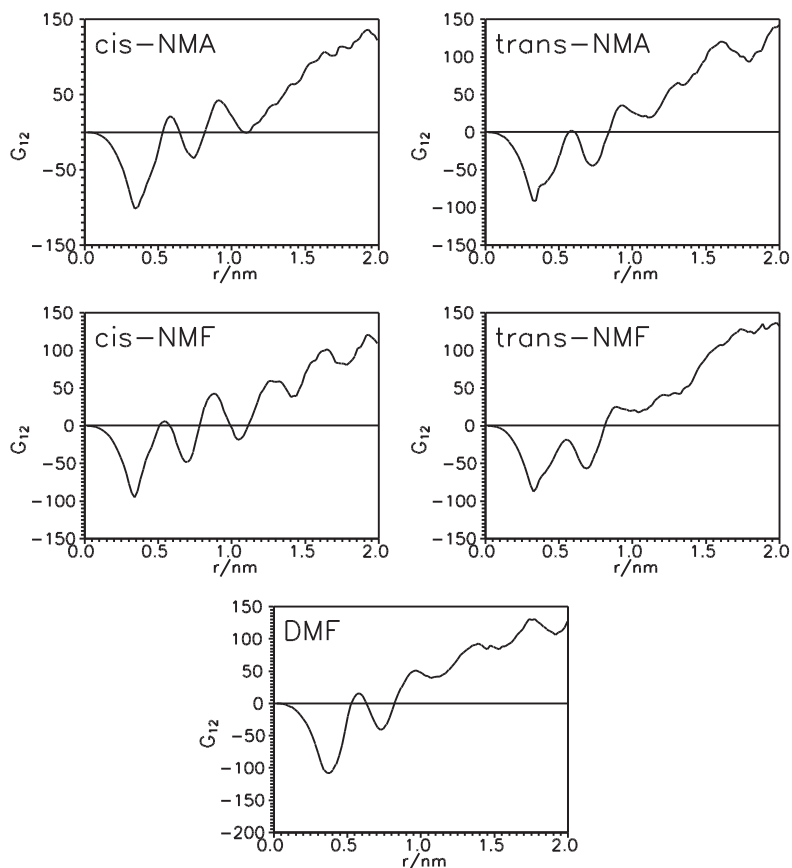


Figure 5. $G_{ij}(r)$ as a function of radius r , calculated from Equation (9)

It is interesting to try to estimate the Kirkwood-Buff integrals from the molecular rdf, and further to compare these with the experimental data. The calculated $G_{ij}(r)$ functions, defined as:

$$G_{ij}(r) = \int_0^r (g_{ij}(x) - 1) 4\pi x^2 dx \tag{9}$$

should be converged asymptotically to the finite value if r increases infinitely. In this limit, the $G_{ij}(\infty)$ value should be equal to the experimental one. Such asymptotic behaviour was observed for the calculated $G_{ij}(r)$, obtained by solving the Percus-Yevick equation – see Figure 1 in the reference [35]. For our systems, however, the $G_{ij}(r)$ functions diverge (Figure 5). This result can be explained as follow: since the $[g_{ij}(x) - 1]$ function in the Equation (9) is multiplied by the factor x^2 prior to the integration, even small deviations (fluctuations) of the $g_{ij}(x)$ value from the unit value give, at large x , large contributions to the G_{ij} value. These fluctuations of the $g_{ij}(x)$ around unity arise as a consequence of the finite number of molecules used in calculations. Then, the divergence of $G_{ij}(r)$ is observed. In our calculations, we used a relatively large number of molecules ($N = 729$) because we expected that convergence should increase with the increasing number of molecules. The results obtained indicate, however, that even 729 molecules are insufficient to calculate the Kirkwood-Buff integrals by integration of the molecular rdf. A similar observation was

Table 4. Calculated values of the Kirkwood-Buff integrals (from obtained in MD simulations the molecular radial distribution functions, and using Equation (10)). Composition of binary mixture $x_{amide} = 0.518$, radius $R_c = 0.65$ nm. All the values are given in the $\text{cm}^3\text{mol}^{-1}$ units

Amide	Conformer	G_{11}	G_{22}	G_{12}
<i>N</i> -methylacetamide	<i>cis</i>	1	-16	0
	<i>trans</i>	-0.5	6.5	-17
<i>N</i> -methylformamide	<i>cis</i>	-35	-14	-35
	<i>trans</i>	-18	22	-48
<i>N,N</i> -dimethylformamide		12	34	-7

Table 5. Values of the Kirkwood-Buff integrals at equimolar composition, calculated from thermodynamic data for the {amide+methanol} binary mixtures at the temperature $T = 313.15$ K. All the values are given in the $\text{cm}^3\text{mol}^{-1}$ units

Amide	G_{11}	G_{22}	G_{12}
<i>N</i> -methylacetamide	-92.2	-31.5	-42.1
<i>N</i> -methylformamide	-63.3	-24.6	-48.0
<i>N,N</i> -dimethylformamide	-92.8	-35.8	-41.1

made by Adams [36] for the simple binary {benzene+argon} mixture: he found that even 864 argon molecules were insufficient for determination of the Kirkwood-Buff integrals by the integration procedure.

We propose here, however, a simple procedure for avoiding this difficulty. Our argumentation is as follows: if the radius of the solvation shell is approximately equal to the radius of the first coordination sphere, the following approximation should be fulfilled [10, 11]:

$$G_{ij} = \int_0^{R_c} (g_{ij}(r) - 1) 4\pi r^2 dr + \int_{R_c}^{\infty} (g_{ij}(r) - 1) 4\pi r^2 dr \approx \int_0^{R_c} (g_{ij}(r) - 1) 4\pi r^2 dr, \quad (10)$$

where R_c symbolizes the radius of solvation shell. The above estimated radius is equal to 0.65 nm approximately – then we can estimate the G_{ij} values. Estimated by this means, the G_{ij} values are collected in the Table 4. Values of the Kirkwood-Buff integrals obtained from experimental data are given in Table 5.

The observed differences between calculated (Table 4) and experimental (Table 5) results can be explained as follows. First, it is quite obvious that this procedure can not produce the exact values of the Kirkwood-Buff integrals. Second, the model used in calculations is an approximate only. For example, a simplifying feature built into this model is the “united atom” approximation. Another approximation is to use a set of fictitious partial charges distribution. These values were fitted to the best reproduction the thermodynamic properties of pure components [29, 30], not the mixture. Calculated molecule-molecule rdf’s depend, of course, on the form of the potential energy of interactions, especially within the first coordination sphere. This is why the differences between calculations and experiment are observed.

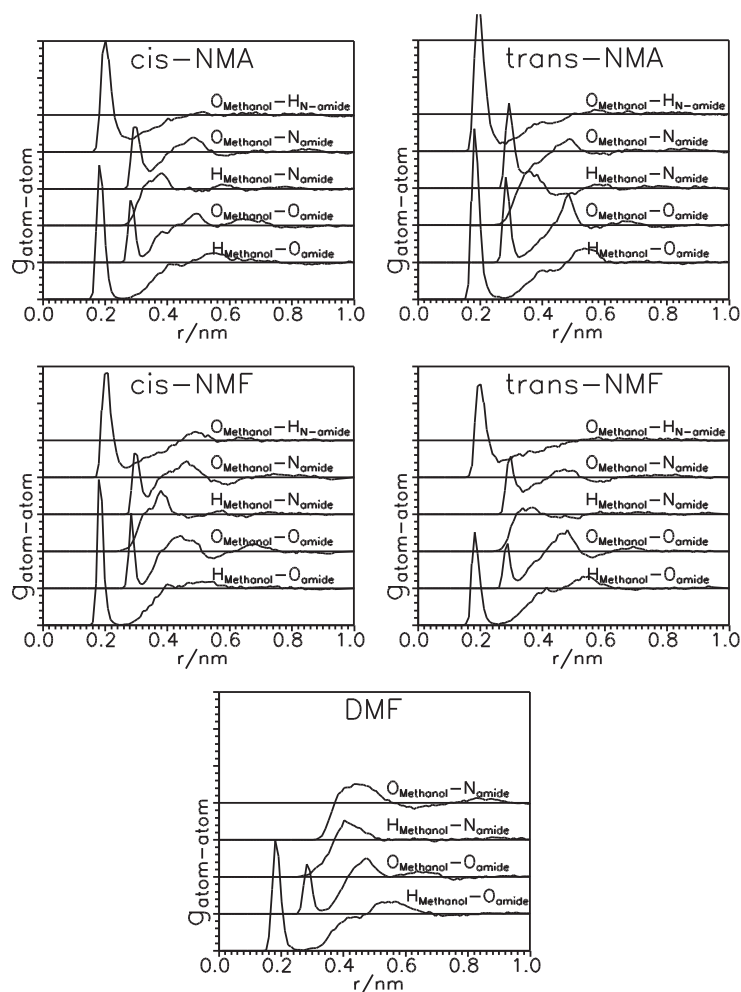


Figure 6. Atom-atom radial distribution functions, calculated for {amide(1)+methanol(2)} binary mixtures

We can say that conclusions derived from molecular rdf agree, in general, with the thermodynamic conclusions. It is visible, moreover, that both: *cis* and *trans* conformers differ; this difference reflects difference in solvation of both conformers by methanol.

In the previous works [2, 37] the orientational entropy was calculated – the entropy changes originating from orientational effects within the solvation shell. These effects result from dipole-dipole interactions and possibility of the hydrogen bond formation between molecules. The $T\Delta S_{orient}$ quantities for {amide+methanol} binary mixtures at equimolar composition and at the temperature 313.15 K are [37]: 93 J·mol⁻¹ for DMF and 116 J·mol⁻¹ for NMF. Unfortunately, there are no experimental data available for the heat of mixing of {NMA+water} and {NMA+alcohol} binary mixtures at $T = 313.15$ K, and, therefore, it is impossible to calculate $T\Delta S_{orient}$ for these systems, especially for the {NMA+methanol} systems. The H^E results for {NMA+water} mixtures at $T = 308.15$ K [38, 39] and at $T = 323.15$ K [40] are the only present in literature, allowing to estimate the orientational

Table 6. Number of amide molecules forming stable complexes in the investigated {amide+methanol} binary mixtures. The limiting value for $H_{\text{methanol}-\text{O}_{\text{amide}}}$ and $H_{\text{N-amide}-\text{O}_{\text{methanol}}}$ distance is equal to 0.23 nm; total numbers of amide and methanol molecules are: 378 and 351, respectively

		$H_{\text{methanol}-\text{O}_{\text{amide}}}$ bond	$H_{\text{N-amide}-\text{O}_{\text{methanol}}}$ bond
<i>N</i> -methylacetamide	<i>cis</i>	51	13
	<i>trans</i>	53	37
<i>N</i> -methylformamide	<i>cis</i>	61	18
	<i>trans</i>	22	13
<i>N,N</i> -dimethylformamide		28	–

effects for this system; the estimated values of $T\Delta S_{\text{orient}}$ are strongly negative, as well as for {DMF+water} binary mixture [2, 37].

The orientational effects should be, nevertheless, visible in the atom–atom radial distribution functions calculated from MD simulations. We take into account the following methanol–amide atom–atom rdf's: g_{HO} , g_{OO} , g_{HN} , g_{ON} and g_{OH} and display these functions in Figure 6. As can be seen, the strong orientational effects around the oxygen atom of the amide are observed for all the investigated amides; as we can expect, the orientation of methanol molecules around the nitrogen atom is less visible. These effects are clearly visible within the solvation shell; within the second coordination sphere they are nearly invisible (Figure 6).

Similar behaviour was observed for the {formamide+water} binary mixture. Recently Puhovski and Rode [41] have carried out simulations of this system, using the polarizable test particle model (T-model) for both formamide and water molecules. They found that the local mole fractions of components around the formamide molecule are nearly equal to the bulk ones, and this result agrees with the experiment. Moreover, orientational effects of water molecules around the formamide molecule were observed: there are significant orientational effects for both water–water and water–formamide interactions, observed at short ranges corresponding to the first solvent shell.

The clearly visible first peak on the methanol–amide g_{HO} rdf indicates the existence of a hydrogen bond between amide and methanol molecules. This hydrogen bond is responsible for the formation of the complexes between these molecules. Thus, we may consider the stable complexes, “living” at least 20 ps (a time of a single simulation run) in the resulting files obtained from MD simulations. The complex we have considered as stable, if the $H_{\text{methanol}-\text{O}_{\text{amide}}}$ distance never exceeds (in the 20 ps interval) the limiting value, assumed to be equal to 0.23 nm (it is position of the first minimum on the methanol–amide g_{HO} rdf); a similar procedure can be applied to the $H_{\text{amide}-\text{O}_{\text{methanol}}}$ hydrogen bond. The results of the research are collected in Table 6. We can say, therefore, that MD simulations confirm the existence of stable complexes in the {amide+methanol} binary mixtures.

Finally, we can say that the picture obtained from the analysis of the molecular dynamics results is consistent with the thermodynamic data and with all deductions derived from these measurements.

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