Specific Intermolecular Interactions of Organic Compounds

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Chapter 2
Nontraditional Approaches to Thermodynamic Analysis of Liquid Organic Compounds

2.1 Consequences of the Essentially Unshared $2s^2$-Electron Pair of Carbon Atom

The structure of the liquid state of one among the simplest compounds, methanol, is regarded as formed by hydrogen bonds involving the hydroxy group. This concept is preserved although a lot of publications discuss this compound [1]. The methyl group of the CH_3OH molecule possessing an essentially unshared $2s^2$-electron pair and a pronounced donor or acceptor properties depending on the interacting functional group in the contacting molecule of the nearest surrounding has valuable features necessary for the understanding of the nature of specific interactions in liquid alcohols, functional solvents, ketones, ethers, and carboxylic acids. The differences in the structures of the liquid organic compounds and their solutions govern directly the nature of the specific interactions which depend on the definite bond vacancy of the molecule, functional group, and evidently on the CH_3-group possessing the mode of the specific interaction inherent to it. The latter originates from the pseudoatomic essentially unshared $2s^2$-electron pair. Therefore the functional solvents, in particular, *N*-methylformamide, whose molecule contains various functional groups of different character, should form in the liquid state versatile types of specific interactions. Hence it is necessary to develop new approach to the investigation of liquid structures and to the analysis of their thermodynamic and other physicochemical properties. Apparently, none of the existing investigation methods provide unambiguous information on the structure of the solution and the solvent. For instance, in the case of close energy values of two specific interactions in solution of dissimilar character it is impossible to determine their structure based only on the spectral data or quantum-chemical calculations [2–4]. The processing of the X-ray pattern for liquids gives reliable information only on the mean number of neighbors in the first coordination shell. However, the X-ray patterns also cannot be solved in case of close energy values of different types of the specific interactions. The investigation of finer details of the structure meets more difficult problems of the ambiguous character of a method [2–4]. The radial distribution function (RDF)

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converts the spatial distribution of atoms and molecules into a smoothed homogeneous function. This approach restricts the possibility to use the concept of molecule for understanding the structure of the short-range ordering in the liquid, e.g., at the formation in the alcohols of the hydrogen bond H-O•••H-O and the specific interactions H–O→CH_3 formed by the essentially unshared $2s^2$-electron pair of the carbon atom from the methyl group in the case of small difference in their energies. At the same time two different configurations, in particular, with the larger energy difference between the hydrogen bond H-O•••H-O and the specific interaction H–O→CH_3, may be described by virtually similar RDFs. This fact restricts the use of the X-ray diffraction for the evaluation of the short-range ordering in liquids. The X-ray diffraction studies extended, for example, the understanding of the structure of the liquid dimethylformamide [5]. Yet the suggested structure did not take into consideration the existence of the specific interactions O→CH_3, N–H_3C←N [6] that should fundamentally correct the assumed structure and also should improve the quantum-chemical calculations of the hydrogen bond energy in liquid formamide amounting according to the calculations to 67.3 kJ mol^{-1} for the chain structure and to 63.2 kJ mol^{-1} for the ring structure [1, 7, 8]. Consequently in the probabilistic structure of liquid, the sp^3-hybridization model of the carbon atom should be rejected and the presence of the essentially unshared $2s^2$-electron pair forming the specific interaction and supplying the carbon atom with the pentacoordinate state should be taken into account. Because of this ability of the carbon atom the methyl group acquires the property of a functional group with a free bond vacancy; this fact is confirmed by the quantum-chemical calculations. It is seen by an example of the dimeric molecule of trimethylaluminum that this functional group enters into coupling chemical interaction between the carbon atom of the methyl group and the aluminum atom of another molecule, and this interaction is strictly localized on the definite orbitals of the reacting species [9]. The pseudoatomic essentially unshared $2s^2$(c)-electron pair of the carbon of the $Al(CH_3)_3$ involved into the interaction with the aluminum atom of a molecule in the nearest surrounding is localized on the p_z-orbital of the aluminum atom. The interaction is of the donor–acceptor character and belongs to the new type of specific interactions Al←CH_3–Al. This type of donor–acceptor interactions extends the concept of the intermolecular interactions. Note that the weak hydrogen bond in the liquid ammonia is also a specific interaction. The same donor–acceptor bond forms the carbon atoms of methyl groups with the metal in the metal alkyls AR_k. The interactions A–R→A are formed between the molecules of the nearest surrounding in the liquid alkylmetals. The presence of the essentially unshared $2s^2$(c)-electron pair in the alkyl derivatives AR_k provides many possibilities of the formation of specific interactions of the same nature, of different types varying by energies and charges on the atoms of elements and carbon. The negative charge on the carbon in the methyl group in trimethylboron B–CH_3 (−0.234) considerably exceeds the charge on the similar group in the trimethylamine N–CH_3 (−0.023) and results in the high energy of the specific interactions B–H_3C→B and N→CH_3–N [10]. Thus, the pseudoatomic $2s^2$(c)-electron pair of the methyl group of trimethylboron is capable of donor qualities, and the methyl group of trimethylamine, of acceptor properties forming the donor–acceptor coupling interactions. Under certain conditions, the methyl groups form less stable interactions $\mathrm{M{-}CH3}^{-\delta}{}_1 \rightarrow \mathrm{CH3}^{-}\delta 2{-}\mathrm{E}\,(-\delta_1 > -\delta_2)$ with existing inequality of the negative charges $-\delta^1 > -\delta^2$.

This type of specific interactions of low stability may arise in the binary systems of metal alkyls [11, 12]. The treatment of the structures of liquid organic compounds becomes complicated with the growing number in the molecule of functional groups whose bond vacancies form the specific interactions. For the multitude of the nonelectrolyte solutions, the concentration concept of Krestov et al. [1] is the most attractive. The concept is based on the dominating structure of the solution components. In the total range of solutions, certain compositions are marked where the structure of the solvent is governed by the structure of the pure components or the structure of their mixtures, solvated molecules of the solvate. The fundamental value of this concept is the admission of the formation of solvated species. The advantage of this concept consists in regarding the system as the product of the interaction of molecules of similar compounds; therefore the solvent molecule with all its bond vacancies dictates the solvate structure. Hence the properties of such solutions originate from the changes in the energy of the specific interactions in the liquid component and the specific interactions newly formed in the solvate. This characteristic feature of the nonelectrolyte solutions restricts the free choice of structures in the interpretation of the observed solution properties as a function of its composition. Inasmuch as the solvation is understood as the sum of energy and structural changes in the process of the solvent molecule transition into the liquid phase of the solution [1], the establishment of the thermodynamic properties of the reverse process makes it possible to evaluate the energies of the specific interactions existing in the solvate using the information on the vapor composition [13, 14]. Obviously, in this case, the energy of specific interactions does not take into account the long-range solvation and the nonspecific interactions. At the analogy of the structure of the liquid component and the solvate, the entropy as a structural characteristic corresponds only to the energy difference in the specific intermolecular interactions arising in the structures of the initial liquid compounds [15].

Nontraditional approaches to the thermodynamic and other physicochemical properties of liquid and solid organic compounds of saturated and unsaturated series, organoelemental compounds, and large compounds with varying number of functional groups, bond vacancies, of nonelectrolyte solutions aimed at the evaluation of the energy of specific interactions, the hydrogen bonds included, are based on the following principles [16–18]:

1. Well-grounded rejection of the model of sp^3-hybridized carbon atom in organic and organoelemental compounds
2. The existence of an essentially unshared $2s^2$(c)-electron pair of carbon atom, the existence of a pentacoordinate carbon atom taking part in the formation of specific interactions
3. All bond vacancies of the molecules of organic compounds participate in the specific interactions

4. The enthalpy (entropy) of sublimation, vaporization, melting, and polymorphous transitions are connected with the number of the broken specific interactions and their energies
5. The dominating influence of the structure of the solution components. Several regions of composition are separated where the solvent structure is defined by the structure of pure components or the solvated species of the mixture [13–15]

Whereas the knowledge of the structure of liquid and solid organic compounds provides the understanding of the thermodynamic properties [7, 8], the knowledge of the thermodynamic characteristics of vaporization makes it possible to evaluate the energies of the specific intermolecular interactions. The fundamentally important point consists in the possibility by well-founded estimation of the bond vacancies of the molecule to get to the evaluation of the energy of the specific interactions employing the enthalpy characteristics of vaporization. In event of liquid water having a tetrahedral structure in the crystal and in the liquid state at the temperature close to the melting point, the molecule has four free bond vacancies forming four hydrogen bonds whose cleavage at the vaporization allows the evaluation from the enthalpy characteristic of vaporization (43.96 kJ mol^{-1}) [5] the energy of the hydrogen bond at 10.99 kJ mol^{-1} [$\Delta_{\text{vap}}H^0$ (298 K)/4]. At the higher temperature, tetrameric and other forms of water molecules with a reduced number in the ring form in the liquid state of water, therefore the hydrogen bond energy is an average value. Taking into account that monomer molecules are going over into the vapor the temperature increase is accompanied by some insignificant stabilization of the hydrogen bond due to the decrease in the number of molecules in the cycle. Still its different energies measured at the nonstandard temperature originate from the difference in the thermal motion. The nonspecific interactions are ignored in the thermodynamic calculations of the energies of the specific interactions and the hydrogen bonds for the energies of nonspecific interactions are as low as the error limits of the experimental measurements of the enthalpy characteristics.

2.2 Specific Interactions of Liquid Alkyls and Their Energies

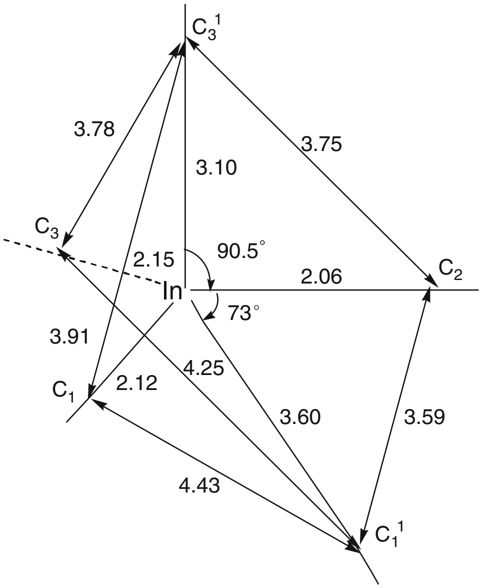
Regarding the structure of a liquid as a unique system whose elementary volume is meaningful when it contains the minimum number of species obeying the statistical laws [1], the knowledge of the number and types of the bond vacancies, of interacting species provides a possibility to estimate the energy of the specific interactions. This interpretation of the structure of the molecular liquid requires definite model concepts incorporating the characteristic features of the initial species. For instance, the evaluation of the energy of the hydrogen bond in liquid water (cited above) required the knowledge of the number of its bond vacancies, of the vaporization enthalpy and the vapor composition. This approach results in a system of self-consistent energies of the specific interactions in molecular liquids.

Here the most important point is the accounting for the structure of the molecule and its bond vacancies. This approach is already applied fundamentally to functional solvents, alcohols, and carboxylic acids. However, for all these compounds only the number of hydroxy or carboxy groups was taken into consideration. The quantum-chemical calculations performed for the evaluation of the energy of the hydrogen bonds also took into account only the OH groups [7, 8]. Therefore, for estimation of the energy of previously unknown types of specific interactions in the molecular liquids of organoelemental compounds we use the above named principles. In this connection let us consider the structure of the molecules of organoelemental compounds, the vapor composition, and the structure of the crystal and the liquid.

Alkylmetals of the zinc subgroup have a linear form [19]. The alkylmetals of the boron subgroup have a structure of planar triangle. The investigations by X-ray and electron diffraction and by IR spectroscopy showed that alkyls of gallium and indium existed in vapor as monomer molecules. The trimethylaluminum is present in vapor in dimers [20, 21], triethylaluminum is less dimerized in vapor [21], and the partial pressure of $Al_2(n\text{-}C_3H_7)_6$ in vapor is incomparably lower [22]. In vapor trimethyl- and triethylaluminum was investigated by X-ray and electron diffraction and by IR spectroscopy [23–26]. The alkylaluminum exists in dimers both in the liquid and in the solid state [27]. The independent electron diffraction studies [11, 12, 19] showed that trimethylindium is a tetramer in the crystal and a monomer in vapor and in liquid. The study of the crystalline trimethylindium by the X-ray diffraction resulted in a conclusion on the existence of a group of four indium atoms and trigonal units $In(CH_3)_3$ located nearly in a plane normal to the plane of In_4. The tetrameric unit is held by the methyl groups placed between the indium atoms. As a result the carbon atom is in the pentacoordinate state [28].

The study of the structure of the trimethylindium crystal [29] furnished the structural parameters and interatomic distances in the distorted trigonal bipyramid (Fig. 2.1) with an indium atom in the center that formed two specific interactions $In\text{-}CH_3 \rightarrow In$ with the molecules of the nearest surrounding and three proper methyl groups with the indium atoms of the same contacting molecules. Consequently, the trigonal bipyramidal structure of the crystal of $In(CH_3)_3$ includes five pentacoordinate carbon atoms. Trimethylthallium also forms analogous crystal structure. The study of the vibration spectrum of trimethylgallium [28, 30] also indicated the presence in the liquid state of dimeric molecules like those of $Al_2(CH_3)_6$. However, the investigation of this compound by X-ray diffraction and IR spectroscopy [30] did not found dimers in the liquid trimethylgallium. The existence of the trimethylaluminum in the dimeric form allows a conclusion that this molecule has four bond vacancies (Fig. 2.2), and the coordination number of the aluminum atom is also four. In the series of alkyl compounds of the aluminum subgroup elements, the number of coordinated molecules grows, and in the liquid and crystal state of alkyl compounds in the series gallium–thallium round the central bipyramidal structure five molecules are coordinated (Fig. 2.2). The metal atom in alkyls of the elements of zinc subgroup MR_2 of the linear structure is capable of acquiring additionally two electron pairs at the contact with the methyl groups of the other molecules

Fig. 2.1 The structure of trimethylindium in solid state



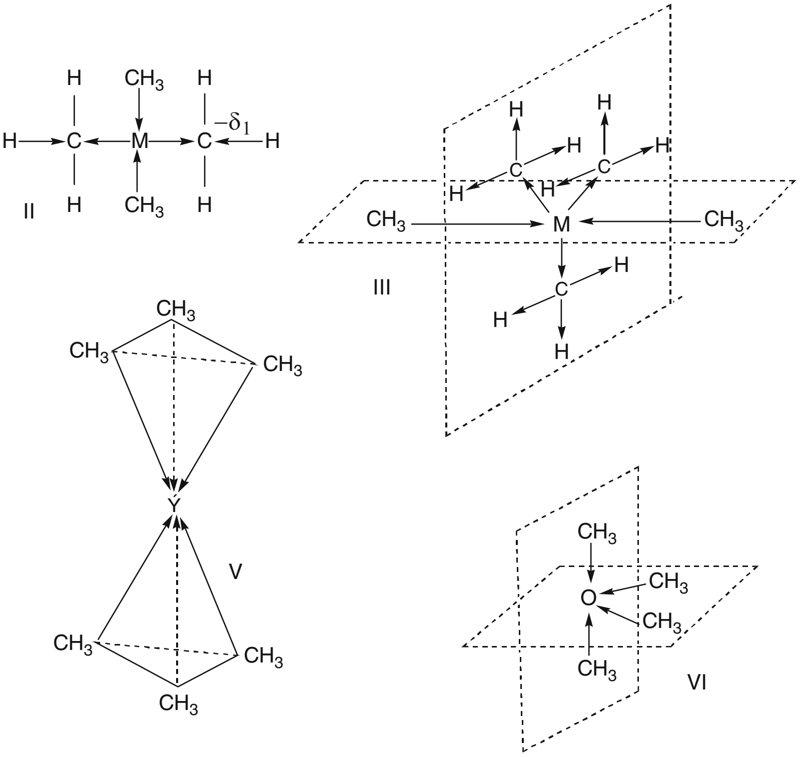


Fig. 2.2 Coordination possibilities of alkyls of the elements of main groups

(Fig. 2.2). The molecules of these alkyl derivatives interact through two CH_3 groups with the metal atoms (M = Zn, Cd, Hg), and two specific interactions $M–CH_3{\rightarrow}M$ are formed by the proper methyl groups.

The information on the liquid and solid state of the alkyl derivatives of elements from the fourth to sixth groups of the periodic table belonging to subgroups of carbon, nitrogen, and sulfur are scanty. From the viewpoint of bond vacancies, the alkyls of the elements from the sulfur subgroup having an angle structure and two unshared electron pairs on the atom of the central element ER_2 form the structure of the liquid state similar to that of water (Fig. 2.2), utilizing four bond vacancies. A similar structure has the alkyls of the nitrogen subgroup. All hydrogen atoms of ammonia NH_3 and carbon atoms of the CH_3 groups of the alkyl derivative ER_3 take part in the formation, respectively, of the hydrogen bonds and the specific interactions, and around the central atom are located six coordinated hydrogen atoms or methyl groups (Fig. 2.2). This is not something extraordinary since all bond vacancies should be occupied, the atoms of the nitrogen subgroup are frequently pentacoordinate, and the formation of complexes with octahedral structure is characteristic of these elements. Note that the central atoms in the alkyls $A(CH_3)_k$ of the elements from the second to fourth main groups bear positive charges and show acceptor properties in the formation of the specific interactions $A–CH_3{\rightarrow}A$ whereas the atoms of the elements of the fifth to sixth main groups $E(CH_3)_k$ possess negative charges and exhibit donor properties in the formation of the specific interactions $E–CH_3{\leftarrow}E$ (Fig. 2.3).

All alkyl compounds of the main group elements form specific interactions involving the pentacoordinate carbon atom (Fig. 2.4). The established bond vacancies of the alkyl compounds of the main group were used in the calculations of the energy of the specific interactions.

The performed calculations of the energy of the specific intermolecular interactions using the vaporization enthalpy [13] show (Table 2.1) that in some events this energy exceeds that of the hydrogen bond in the liquid water (10.99 kJ mol^{-1}) and essentially exceeds the energy of the same type interaction in the liquid ammonia (3.89 kJ mol^{-1}). Note that in the performed calculations the nonspecific interactions of low stability were disregarded for their values do not exceed the error in the experimentally measured thermodynamic characteristics.

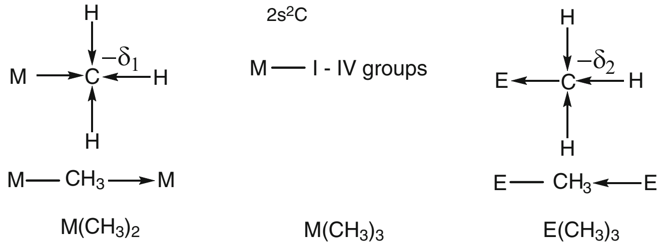


Fig. 2.3 Donor and acceptor properties of carbon atom in methyl group of alkyl compounds

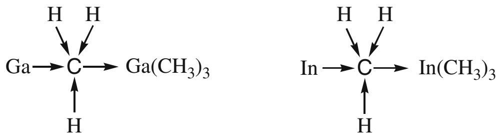


Fig. 2.4 Pentacoordinate carbon atoms in a specific intermolecular interaction

Table 2.1 Energies (kJ mol^{-1}) of specific interactions in liquid alkyls of elements of main subgroups

Compound	Bonding	Energy $DM–CH_3\rightarrow M$	Compound	Bonding	Energy $DE–CH_3\leftarrow E$
$Zn(CH_3)_2$	$Zn–CH_3\rightarrow Zn$	7.60	$C(CH_3)_4$	$C–CH_3\rightarrow C$	2.36
$Cd(CH_3)_2$	$Cd–CH_3\rightarrow Cd$	5.22	$Sn(CH_3)_4$	$Sn–CH_3\rightarrow Sn$	4.08
$Hg(CH_3)_2$	$Hg–CH_3\rightarrow Hg$	8.32	$N(CH_3)_3$	$N–CH_3\leftarrow N$	4.25
$Zn(C_2H_5)_2$	$Zn–C_2H_5\rightarrow Zn^a$	9.70	$P(CH_3)_3$	$P–CH_3\leftarrow P$	4.80
$Cd(C_2H_5)_2$	$Cd–C_2H_5\rightarrow Cd^a$	9.48	$N(C_2H_5)_3$	$N–C_2H_5\leftarrow N^b$	5.86
$Al(CH_3)_3$	$Al–CH_3\rightarrow Al$	10.30	$O(CH_3)_2$	$O–CH_3\leftarrow O$	5.75
$Ga(CH_3)_3$	$Ga–CH_3\rightarrow Ga$	8.42	$S(CH_3)_2$	$S–CH_3\leftarrow S$	7.09
$In(CH_3)_3$	$In–CH_3\rightarrow In$	8.42	$Se(CH_3)_2$	$Se–CH_3\leftarrow Se$	7.80
$Al(C_2H_5)_3$	$Al–C_2H_5\rightarrow Al^a$	12.70	$O(C_2H_5)_2$	$O–C_2H_5\leftarrow O^b$	8.13
$Ga(C_2H_5)_3$	$Ga–C_2H_5\rightarrow Ga^a$	8.78	$S(C_2H_5)_2$	$S–C_2H_5\leftarrow S^b$	8.74

[a] $M–CH_2–CH_3\rightarrow M$

[b] $E–CH_2–CH_3\leftarrow E$

The regularity of energy variation of the considered specific interactions in the series of the main group elements is conserved in the methyl and methyl–ethyl derivatives. The sufficiently low errors in the experimentally measured vaporization enthalpies of alkyls of the elements from the second, third, and fifth groups [13] suggest that the deviation from the regular character in the energy variation of the specific interactions in alkylcadmium, alkylgallium, and alkylphosphorus has a profound sense. We believe that the cause of this fact consists in the electronic population of p_z-orbital of the elements of the main groups and the specific capability of the carbon atom to exhibit donor or acceptor properties depending on the properties of the other element involved in the intermolecular interaction.

The location of various numbers of electrons on dissimilar energy levels results in different donor properties of cadmium and gallium atoms. The presence of five electrons on the third energy level of the phosphorus atom provides it with acceptor properties in the interaction with the carbon atom. Thus, the carbon atom with an essentially unshared $2s^2$-electron pair exhibits the acceptor properties with the zinc and gallium atoms and, on the other hand, donor properties with the phosphorus atom. It is symptomatic that the comparative analysis of the electronic structures of the molecules of $B(CH_3)_3$ and $Al(CH_3)_3$ (Chap. 1), obtained from the X-ray data, shows the smaller contribution of the $Al3p_z$-orbital into the π-molecular orbital and an enhanced positive charge on the aluminum atom [31]. In dimethylmercury of the zinc subgroup, a fundamentally different succession of the 3d-levels is observed. Therefore, the dimethylmercury deviates from the regular series in the energy of the specific interactions having a low value of $Hg–CH_3\rightarrow Hg$ (8.32 kJ mol^{-1}). The alkyl compounds of all elements from the main groups obey the general rule. The energy of the specific interactions grows with the growing number of carbon atoms in the alkyl chain (Table 2.1). However, this growth cannot go on forever, and in going to the compound with larger number of atoms in the chain the energy difference of the intermolecular interactions diminishes in each subsequent step. It is proved on the alkyls of zinc and gallium.

$$\begin{aligned} &\mathrm{DZn(CH_3)_2}(7.60) < \mathrm{DZn(C_2H_5)_2}(9.70) < \mathrm{DZn}(n-\mathrm{C_3H_7})_2(10.53)\\ &\quad < \mathrm{DZn}(n-\mathrm{C_4H_9})_2(12.67) < \mathrm{DZn}(n-\mathrm{C_5H_{11}})_2\left(12.33\,\mathrm{kJ\,mol^{-1}}\right)\end{aligned}$$

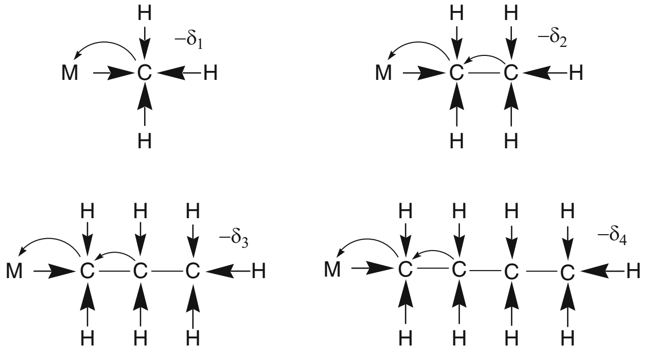
$$\Delta\mathrm{D\ M{-}CH_3 \rightarrow M}\quad 2.10\quad 0.83\quad 2.14\quad -0.34\,\mathrm{kJ\,mol^{-1}}.$$

$$\begin{aligned} &\mathrm{DGa(CH_3)_3}(6.60) < \mathrm{DGa(C_2H_5)_3}(8.78) < \mathrm{DGa(C_3H_7)_3}(9.32)\\ &\quad < \mathrm{DGa(C_4H_9)_3}\left(10.32\,\mathrm{kJ\ mol^{-1}}\right)\end{aligned}$$

$$\Delta\mathrm{D\ Ga{-}CH_3 \rightarrow Ga}\quad 2.18\quad 0.54\quad 1.0\,\mathrm{kJ\,mol^{-1}}.$$

Yet the difference in the energies of the specific interactions is always smaller between compounds with even and odd number of carbon atoms in the alkyl chain than between compounds with the odd and even number of carbon atoms in the alkyl chain. Similar sequence is observed for the dissociation energy of the M–C bond in the series of the alkyl derivatives of an element. This phenomenon is due to the different influence of the reverse dative bond on the energy of the specific interactions at the growing number of carbon atoms in the chain. This means that the shift of the electron density along the chain from the central atom to the terminal methyl group in compounds AR_k of the elements from the subgroups of zinc and boron and along the carbon–carbon chain to the central atom of the fifth and sixth groups in the complex ER_k depends essentially on the even or odd number of carbon atoms in the chain. Consequently, the action of the reverse dative bond between the central atom of the alkyl compound and the contiguous carbon atom essentially depends on the number of atoms in the chain and on whether this number is even or odd (Fig. 2.5).

The sharp decrease in the difference in the vaporization enthalpies at three carbon atoms in the chain shows that the influence of the reverse dative bond is finished and, on the other hand, the trend in the increasing energy of the specific interactions. Although the information on the charges on the central atoms of the compounds in question and on the carbon atoms of the alkyl chains is very scanty, nonetheless, it is illustrative that the charge on the mercury atom in the dimethylmercury (+0.023) turns to negative in $Hg(i\text{-}C_4H_9)_2$ (−0.070) [31]. In this connection should be noted the change in the sign of the charge of the phosphorus atom in going from PH_3 (−0.04) to $P(CH_3)_3$ (+0.070) [31], corresponding to the effect of the reverse dative bond at replacing the hydrogen by the methyl group in these compounds. These data clearly show the opposite direction of the reverse



$$-\delta_1 < -\delta_2 < -\delta_3 < -\delta_4$$

$$D_{1\,M\text{-}C} > D_{2\,M\text{-}C} > D_{3\,M\text{-}C} > D_{4\,M\text{-}C}$$

Fig. 2.5 Decrease in the influence of dative bond with growing number of carbon atoms in alkyl chain on the dissociation energy DM–C and the energy of specific intermolecular interactions

dative bond in the alkyls of the elements of second to fourth groups compared to the elements of the fifth and sixth groups. Note also the decrease in the influence of the reverse dative bond at replacement of the methyl group by ethyl and further propyl group. However, the participation of the pentacoordinate carbon atom in the specific interactions is common for all alkyl compounds.

2.3 Novel Approaches to the Thermodynamic Analysis of Liquid Functional Solvents and Energies of Specific Interaction

It was shown in the preceding paragraph by an example of the alkyl derivatives of the elements of the main groups that the knowledge of the structure of a molecule and of a number of the free bond vacancies is required for understanding the structure of the liquid state of organic compound and the types of the specific interactions. In turn the knowledge of the thermodynamics of the vaporization provides a possibility to establish the energy of the latter for the enthalpy (entropy) of various phase transitions are connected with the energy and the number of the specific interactions [15]. Therefore, the thermodynamic characteristics of the phase transitions cannot be governed by the molecular mass and even in the homologous series the specific features in the intermolecular interactions should be taken into consideration. However even in alkanes appear some complications. For instance, their melting points as a function of the number of carbon atoms in the carbon–carbon chain are described by two plots $T_{\mathrm{m.p.}} = f(n)$ (Fig. 2.6).

As seen from the figure, the melting point grows with the chain length, and the difference of these values in the neighboring members of the homologous series is

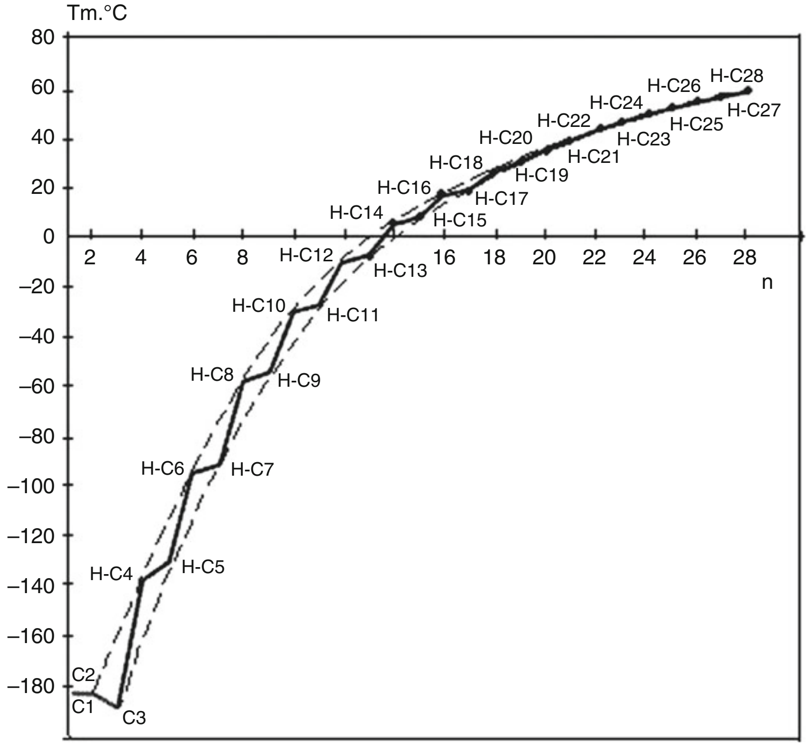
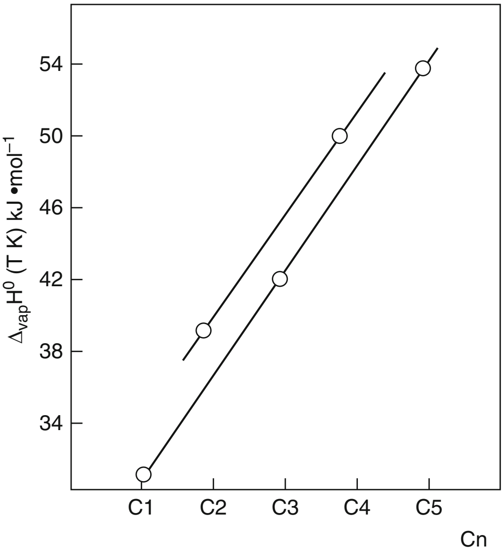


Fig. 2.6 Dependence of the melting points of alkanes on the number of carbon atoms in the molecular chain

not very large. The characteristic crystal lattice of hydrocarbons with even number of atoms n-C_6–n-C_{20} is triclinic. The compounds with a large number of carbon atoms in the chain undergo polymorphous transitions. Their low-temperature phase in alkanes of the series n-C_{20}–n-C_{26} is characterized by the triclinic crystals, and for compounds n-C_{26}–n-C_{36}, the monoclinic modification. The high-temperature phase is stable till the melting point and it possesses a hexagonal structure. The alkanes with the odd number of carbon atoms from n-C_9 till n-C_{35} undergo polymorphous transitions. They have the rhombic structure at low temperatures and the hexagonal one at high temperature. The vaporization enthalpies of the saturated alcohols of the normal structure also should be described by two converging curves corresponding to compounds with even (1) and odd (2) number of carbon atoms in the chain. This feature of alkanes properties is governed by the essentially unshared $2s^2$(c)-electron pair of the carbon atom involved into the distribution of the electron density. Figure 2.7 illustrates two analogous dependences of zinc alkyls where the alkyl substituents contain either even carbon atoms, $Zn(C_2H_5)_2$ and $Zn(C_4H_9)_2$ [33], or odd carbon atoms, $Zn(CH_3)_2$, $Zn(C_3H_7)_2$, $Zn(C_5H_{11})_2$.

Analogous but less pronounces character have the dependences of the vaporization enthalpies of the saturated hydrocarbons (Fig. 2.8). The vaporization entropy

Fig. 2.7 Dependence of the vaporization enthalpy on the number of carbon atoms in molecules of zinc alkyls [32, 33]



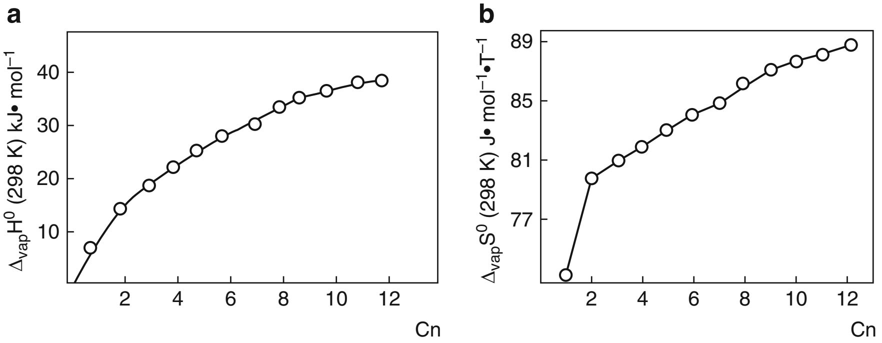


Fig. 2.8 The dependence of the vaporization enthalpy (**a**) and entropy (**b**) on the number of carbon atoms in molecules of saturated hydrocarbons $_{vap}S^0$(298 K) J mol^{-1} T^{-1}

being the characteristic of the structural transformations has a monotonic regularly growing value in compounds C_2–C_{10} illustrating the growing number of broken interactions with the increase of the amount of the CH_2 groups in the molecules.

The dependence of vaporization enthalpy of the alcohols of the normal structure (Fig. 2.9) should be divided in two parts. The first members of this homologous series, methanol, ethanol, and *n*-propanol possess an expressed capability of dimerization in the condensed and vapor phase, and *n*-butanol–*n*-decanol whose properties fit to two converging plots corresponding to the compounds with even and odd number of carbon atoms in the chain. The entropy, structural characteristic with a maximum at the *n*-propanol also indicates that the pronounced ability to dimerize in solid, liquid, and vapor phase is not characteristic of the alcohols of the

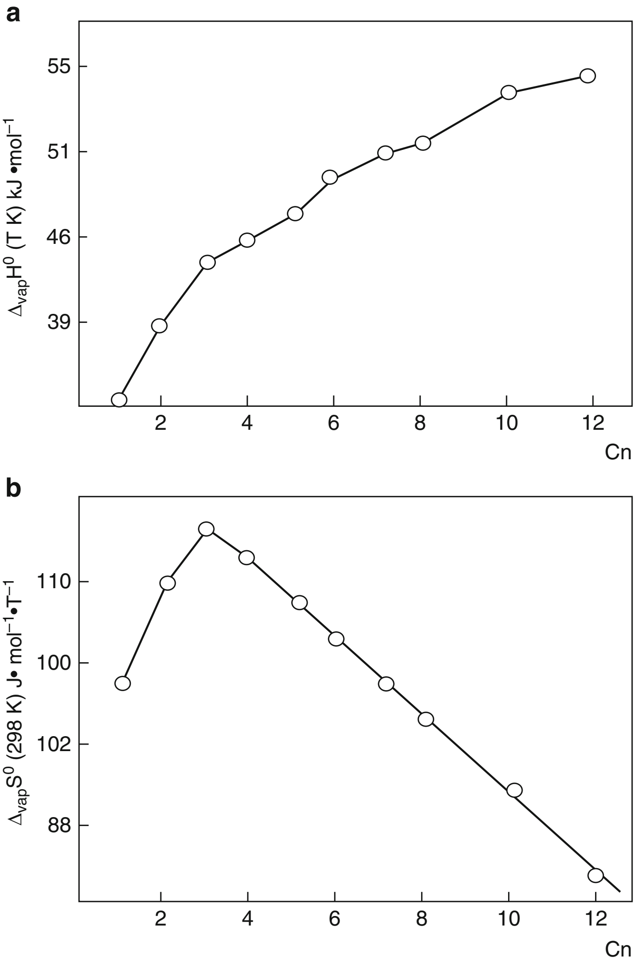


Fig. 2.9 Dependence of the vaporization enthalpy (**a**) and entropy (**b**) on the number of carbon atoms in molecules of alcohols

normal structure with over four carbon atoms in the alkyl chain (Fig. 2.9). If only the hydrogen bonds analogous to those for the homologous series of *n*-alkanes. Yet these two classes of organic compounds are distinguished by the opposite shift of the electron density in the molecules, and by the influence of the reverse dative bond on the formed hydrogen bonds and specific interactions.

Even more drastic inconsistency between the properties of compounds and the value of the molecular mass appear in formamide and its methyl derivatives as show the data of Table 2.2. The growth of the molecular mass in the series formamide < *N*-methylformamide < *N*,*N*-dimethylformamide is accompanied with the decreasing energy of the hydrogen bond as has been revealed by the method of the electron diffraction [8]. In this connection, the influence of the

Table 2.2 Physicochemical properties of compounds [5]

Compound	Molar mass	$T_{\text{m.p.}}$(°C)	$T_{\text{b.p.}}$(°C)	$\Delta_{\text{vap}}H^0$ (298 K)(kJ mol^{-1})
H_2O	18	0.0	100	43.94
CH_3OH	32.04	−97.68	64.35	37.43
AN	41.05	−43.84	81.60	32.9
FA	45.04	2.55	210.5	64.98
C_2H_5OH	46.07	−114.49	78.29	42.31
AC	58.09	−94.7	56.07	29.0
NMF	59.07	−3.8	180	56.25
DMF	73.09	−60.43	153.0	47.51
DMSO	78.13	−43.84	189.0	52.88

methyl group should be analyzed when it replaces a hydrogen atom in the amino group, or, more rightly, at the replacement of the hydrogen bond formed by the hydrogen of the amino group by the intermolecular interaction formed by the methyl group.

Proceeding from the curve of the radial distribution, Ohtaki and Iton [8] concluded that in liquid and crystals the molecular surrounding includes chain, ring, and ring–chain structures [5, 7, 8]. Just the simultaneous presence of chain and ring structures in the liquid formamide can provide understanding of discrepancies in the relaxation and vibration studies (Fig. 2.10).

According to quantum-chemical calculations [5], the hydrogen bond energy in the chain structure (67.8 kJ mol^{-1}) is somewhat higher than that in the ring structure (63.9 kJ mol^{-1}). At the same time it was noted that the presence of two hydrogen bonds in the ring structure provides it with a higher stability. Thus, the chain structure allows the isolation of a dimer with the above hydrogen bond energy D=O · · · H–N– (Fig. 2.10).

In keeping with the concepts of Ohtaki and Iton [8], the considered hydrogen bonds in the liquid formamide and *N*-methylformamide form between the oxygen and hydrogen atoms of amino groups belonging to the contacting molecules $=\text{O}\cdots\text{H–N–}$, which are insignificantly weaker in the NMF with a mobile chain structure. Whereas the curve of the radial distribution established for liquid formamide showed the presence of large wide peaks at 350–550 and 700–900 pm corresponding to strong intermolecular interactions and a considerable molecular order, in the *N*-methylformamide the analogous curves of the radial distribution indicated the absence of a significant range of the intermolecular interactions despite the formation of the strong hydrogen bonds between the molecules. Based on the values of the energy of the hydrogen bonds calculated by the method of molecular orbitals, Ohtaki et al. concluded that the *trans*-position of the hydrogen atom with respect to the methyl group is more favorable than the *cis*-position, and the bond angle $-\text{C=O}\cdots\text{H}-\text{N}-$ equal 120° is also more favorable for the formation of hydrogen bonds between *trans*-positions of the molecules. At the small difference in the energy of molecules and various dimers, the hydrogen bonds of the *N*-methylformamide molecules can form various configurations of the type “head-to-tail” of the linear polymers.

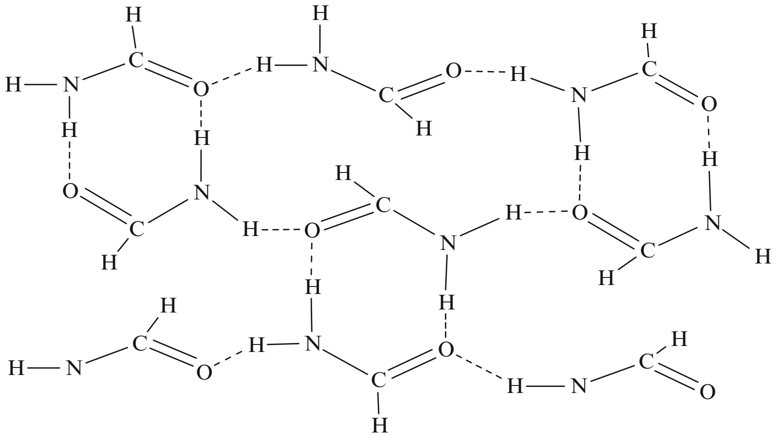


Fig. 2.10 Hydrogen-bonded network structure of liquid formamide [5]

The curves of the radial distribution obtained for *N*,*N*-dimethylformamide [5] showed the absence of any significant peak at $r = 300$ pm. Therefore, Ohtaki et al. concluded that in *N*,*N*-dimethylformamide existed an intermolecular interaction with an interatomic distance around 300 pm and that the interactions $\mathrm{H{-}C{=}O} \cdots \mathrm{H{-}C{=}O}$ did not exist in DMF. Hence they suggested the existence of an intermolecular interaction $\mathrm{H{-}C{=}O} \cdots \mathrm{H{-}C{=}O}$ in liquid DMF weaker than the common hydrogen bond. This suggestion was based on a small positive charge on the hydrogen atom (that was capable to have even a small negative charge), the interatomic distance $r\mathrm{C{-}H} \cdots \mathrm{O}{=}315-335\,\mathrm{pm}$, and the angle $-\mathrm{C{=}O} \cdots \mathrm{H} = +30-(-30)$ [34]. In this connection, the molecules of the *N*,*N*-dimethylformamide can form a chain or network structure with two coordinated molecules. It was noted that the interaction $-\mathrm{COH} \cdots \mathrm{H_3CNH}$ in the liquid *N*,*N*-dimethylformamide has an extremely low stability. The interpretation of the curves of the radial distribution of formamide, *N*-methylformamide, and *N*,*N*-dimethylformamide [5, 35] resulted in a conclusion that in the ring structure of the liquid state of FA six hydrogen bonds $-\mathrm{C{=}O} \cdots \mathrm{H{-}N}-$ of high stability were formed, in the chain structure of NMF two hydrogen bonds of the same type but with reduced stability were formed, and in the chain-network structure of DMF two hydrogen bonds arose [5] $\mathrm{H{-}C{=}O} \cdots \mathrm{H{-}C{=}O}$ of low stability. Regarding the vaporization enthalpy as connected to the number and energy of the hydrogen bonds we calculated the energies of these interactions (Table 2.3). The obtained hydrogen bond energies with a maximum value in NMF are in conflict with the conclusions based on the analysis of radial distribution curves. The obtained sequence is conserved also when the contribution of the weak interactions $-\mathrm{COH} \cdots \mathrm{H_3CNH}-$ and $-\mathrm{COH} \cdots \mathrm{H_3CN}-$ into the vaporization enthalpy of NMF and DMF, respectively, is taken into account. Thus, each assumption gets in conflict with the main conclusions based on the analysis of radial distribution curves of liquid FA, NMF, and DMF.

Table 2.3 Energy of assumed hydrogen bonds obtained from the vaporization enthalpy (kJ mol^{-1})

Compounds	$\Delta_{\text{vap}}H^0$ (298 K)	Hydrogen bond	*D*
FA	64.98	$-\text{C}=\text{O}\cdots\text{HN}- = \Delta_{\text{vap}}\text{H}^0(298\,\text{K})/6$	10.83
NMF	56.25	$-\text{C}=\text{O}\cdots\text{HN}- = \Delta_{\text{vap}}\text{H}^0(298\,\text{K})/2$	28.13
DMF	46.89	$-\text{HC}=\text{O}\cdots\text{HC}=\text{O} = \Delta_{\text{vap}}\text{H}^0(298\,\text{K})/2$	23.45

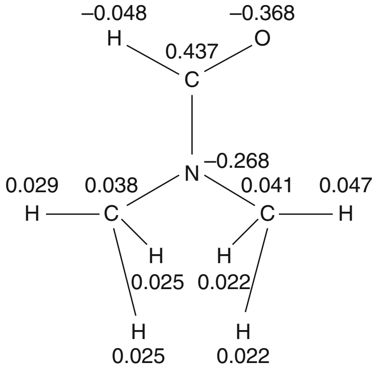


Fig. 2.11 Charge distributions in dimethylformamide

It is not unexpected for Ohtaki et al. have not possessed the additional information, and the conclusion on a small positive charge and even a small negative charge on the hydrogen atom is not right.

This discrepancy between the hydrogen bond energy and the analysis of the curves of the radial distribution is removed at the use of the nontraditional approach to the thermodynamic analysis of the interactions in liquid organic compounds formulated in Sect. 2.1. This approach is based on the rejection of the sp^3-hybridization model and on involvement of the carbon atom of the methyl group into the intermolecular interactions.

First of all note the low values of the positive charges on the hydrogen atoms of the methyl groups in the dimethylformamide (0.025, 0.025, 0.029 and 0.022, 0.028, 0.041) (Fig. 2.11). On this basis a conclusion was made [5] on the formation of very weak intermolecular interactions $-\text{COH}\cdots\text{H}_3\text{CN}-$ and $-\text{COH}\cdots\text{H}_3\text{CNH}-$ in the liquid *N*-methylformamide and *N*,*N*-dimethylformamide. However, this suggestion is dubious. In this connection, the attention is attracted by the high negative charge on the oxygen of the carbonyl group commeasurable with the charge on the oxygen in alcohol or ketone, and by the positive charges on the carbon atoms of the methyl groups.

The possible existence of weak hydrogen interactions $-\text{C}{-}\text{H}\cdots\text{O}-$ was suggested for hydroxy-containing organic compounds [35] between the hydrogen of a methyl group and the oxygen of a hydroxy group. From the analysis of the experimentally observed bands of the stretching vibrations of different bonds in gaseous and liquid methanol [36], it was concluded that in CH_3OH a mean content of such bonds was one per molecule. It was also indicated that these type bonds should be ten times weaker than the ordinary hydrogen bonds of methanol. Hobza and Sponer [37] suggested that the formation of this type of hydrogen bond occurred through nontraditional mechanism of the electron density redistribution and was accompanied with somewhat unusual spectral effects. These so-called nontraditional hydrogen bonds led to the blue shift in the spectra [38]. The performed quantum-chemical calculations of the methanol dimers linked by the classic hydrogen bonds $\text{H–O}\cdots\text{O–H}$ led Vandach et al. to the assumption that the methanol molecule is capable to form the hydrogen bond through the proton of the hydroxy group and that this type of a bond resulted in the blue shift in the corresponding IR spectra [39]. The quantum-chemical calculations using the density functional theory [40] indicate that this bond should decrease the cooperative effect in the liquid methanol. The comparison of the results of the calculations of the monomer structure [40] (bond lengths in the molecule, bond and torsion angles), electron density on atoms, and spectral characteristics showed the inequality of the protons in the methyl group of the methanol molecule. The characteristics of the proton situated in the *trans*-position with respect to the hydrogen of the hydroxy group are distinguished from the characteristics of two other protons of the methyl group. The energy barrier to the rotation of the CH_3-group in the gas phase amounts approximately to 4 kJ mol^{-1} [40]. However, the assumption on a large barrier to rotation in the condensed phase of methanol is not valid for in liquid and solid phase the energy of each interaction decreases due to the coordination effect and larger number of the interactions with the molecules of the nearest surrounding. Therefore for liquid and solid methanol with its characteristic hydrogen bonds and high capability to dimerize in vapor, the energies of the interactions of low stability under consideration should be lesser than 4 kJ mol^{-1}. Thermodynamic analysis of the hydrogen bonds in various classes of organic compounds [41] in the liquid state showed that this type of interactions is approximately tenfold stronger that the nonspecific interactions. For the substantiation of formed interactions, we shall use the information on the participation in complexing of the compounds in question.

The important problem for the thermodynamic consideration of formamide, *N*-methylformamide, and *N*,*N*-dimethylformamide is the understanding of their coordination ability which provides the information on the number of bond vacancies, types of the hydrogen bonds, and the specific interactions. In this connection, the ability of these compounds to form complexes with hydrogen fluoride and hydrogen chloride [42] is especially interesting.

The energy of H-bonds in complexes $(HF)m$DMF at the mixing enthalpy of initial components ~20.9–188.4 kJ mol^{-1} varies in a wide range and is governed by the reciprocal position of the molecules. Among the complexes containing equal number of molecules, the most stable are the complexes with a single molecule of dimethylformamide. The addition to it of more HF molecules occurs with the highest energy gain. The results of performed studies using IR spectroscopy, quantum-chemical calculations, and densimetry are well consistent [43]. The comparison of these studies with those performed for the system HCl–DMF by spectral methods and calculations shows that the results obtained are analogous. These results allow drawing conclusion, that DMF forms exclusively stable heterocomplexes with hydrogen fluoride and chloride [43-45] in all range of concentrations where the coordination number of DMF was 4, 5, and 6. Consequently, the two unshared electron pairs of the oxygen possess two bond vacancies and are involved into the interactions with the molecules of hydrogen fluoride or chloride forming stable hydrogen bonds $-O \cdots H-F$. Less stable interactions are formed by the carbon atoms of the methyl groups attached to nitrogen, N–CH_3. In this connection, let us turn to the electron population in the ammonia molecule (N: $s = 0.515$; $2p_x$, $2p_y = 1.210$; $2p_z = 1.867$; H: 0.734) and in $N(CH_3)_3$ ($N = +0.024$; $C = -0.113$; $H = +0.035$). Note also that the hydrogen bond in the liquid ammonia ($DN \cdots H-N- = 3.9\,kJ\,mol^{-1}$) at a higher positive charge on the hydrogen atom has reduced stability compared with the specific interaction ($DN–CH_3 \leftarrow N = 4.20$ $kJ\,mol^{-1}$) in the liquid $N(CH_3)_3$. This means that the donor properties of the nitrogen atom and the electron density granted to the hydrogen atoms of ammonia are essentially reduced. At the same time in the molecule $N(CH_3)_3$ the positive charge on the nitrogen atom and the negative charge on the carbon correspond to the distribution of the electron density with the participation of the reverse dative bond and giving over of the electron density from the p_z-orbital of the nitrogen. Consequently, the essentially unshared $2s^2$-electron pair of the carbon atom formed a more stable specific interaction than the hydrogen atom of the ammonia molecule. This shows directly that the methyl group forms a specific interaction of the stability higher than the hydrogen bond in the liquid ammonia. The presence of a negative charge on the carbon atom of the methyl group (-0.113) and of a positive charge on the nitrogen atom (+0.023) indicates directly that the positively charged hydrogen atom of the HF molecule predominantly interacts with the carbon atom of the methyl group.

Among the existing complexes, the more stable is the complex containing a single DMF molecule. The most stable are the quasisymmetric hydrogen bridges $O \cdots H-F$ formed by the carbonyl oxygen atom. The main trend in complexing in the system HF–DMF consists in the addition to the cyclic fragment $(HF)m$DMF ($m = 1$–7) of successive HF molecules. The cyclic complexes have both purely cyclic and branched structures. The latter complexes are cycles with added to them "tails" of hydrogen fluoride molecules. In the formed four-nuclear complexes, the quasisymmetric hydrogen bridges $O \cdots H-F$ occupy two bond vacancies and form the cyclic fragment $(HF)m$DMF ($m = 1$–7), and the remaining four vacancies form with the "tail" HF molecules the intermolecular interactions of lower energy. Inasmuch as the oxygen atoms of the carbonyl groups (C=O) of the *N*,*N*-dimethylformamide (Fig. 2.12), *N*-methylformamide, and formamide possess enhanced negative charge and two bond vacancies of two unshared electron pairs, the oxygen atom is capable of the formation of two more stable hydrogen bonds or specific interactions. Therefore, the common feature of these compounds is the ability to form a stable hydrogen bond $-H–C{=}O \cdots H–C{=}O$.

The presence in the molecule of *N*,*N*-dimethylformamide of two methyl groups results in the formation of two specific interactions with coordinated molecules of the hydrogen fluoride. The fifth coordination bond originates from the nitrogen atom forming it with the hydrogen of the HF molecule. The last coordination bond is formed by the hydrogen of the fragment (O=)C–H possessing higher

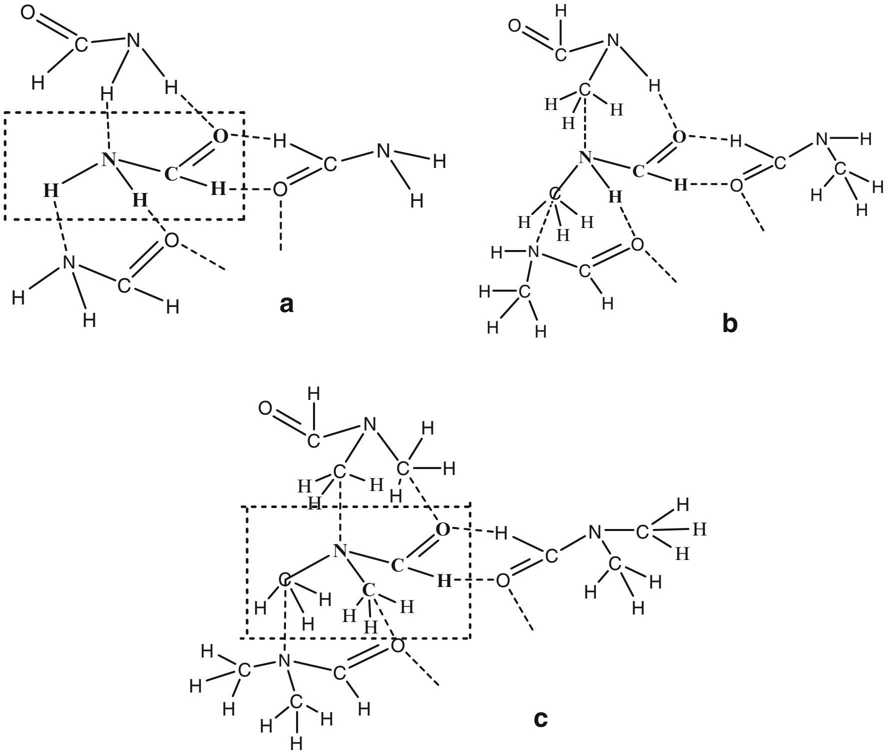


Fig. 2.12 Schematic pictures of hydrogen bonds and specific intermolecular interactions in liquid FA (**a**), NMF (**b**), and DMF (**c**)

positive charge than the hydrogen atoms of the methyl groups. A similar sequence of hydrogen fluoride molecules addition corresponding to the regular decrease in the stability of formed interactions exists in the complex formation with *N*-methylformamide and formamide. Consequently, the liquid functional solvents FA, NMF, and DMF are complex systems which utilizing six bond vacancies form various types of hydrogen bonds and specific interactions with characteristic energy values.

Thus, the sequence of the hydrogen fluoride coordination in its complexing with *N*,*N*-dimethylformamide shows the enhanced stability of the specific interaction formed by the essentially unshared $2s^2$-electron pair of the carbon atom of the methyl group and the unshared electron pair of the oxygen atom $N–CH_3 \leftarrow O{=}C(H)$. The second type of the specific interactions with lower stability is formed by the analogous methyl group and the unshared electron pair of the nitrogen atom $N–CH_3 \leftarrow N$. The schematic picture of the structure of liquid FA, NMF, and DMF with the coordination of three molecules shown in Fig. 2.12 depicts three types of six hydrogen bonds and specific interactions forming cycles linked into a network by interactions of various stability.

The formamide molecule with two NH_2 groups and six bond vacancies forms three types of hydrogen bonds in the liquid state: H–C=O···H–C=O (two), N–H···N (two), and N–H···O (two) (Fig. 2.12a). One such type of hydrogen bonds forms in liquid *N*-methylformamide, another in *N*,*N*-dimethylformamide.

The molecule of the *N*-methylformamide coordinates three molecules and forms two types of hydrogen bonds, H–C=O···H–C=O (two) and N–H···O=C–H (two), and two specific interactions *N*-CH_3←N (Fig. 2.12b). In keeping with the curve of the radial distribution, the second type of hydrogen bonds possesses a reduced stability as compared with the hydrogen bonds in the liquid formamide. The hydrogen atom of the NH-group forms the third type of the hydrogen bond N–H←N of lower stability with the nitrogen atom of the molecule in the nearest surrounding. The distinguishing feature of the *N*,*N*-dimethylformamide with two methyl groups is the formation in the liquid state of two types of the specific interactions through the methyl groups, H–C=O→CH_3–N (two), N–CH_3←N (two), and of two hydrogen bonds H–C=O···H–C=O (Fig. 2.12c). A significant distinguishing feature of liquid *N*-methylformamide and *N*,*N*-dimethylformamide is the formation of the specific interactions N–CH_3←N existing in the liquid trimethylamine (4.25 kJ mol^{-1}) with the energy exceeding that of the hydrogen bond in the liquid ammonia (3.89 kJ mol^{-1}). Note that it was shown by X-ray electron spectroscopy that the replacement of hydrogen in ammonia by a methyl group leads to insignificant decrease in the electron density shift to the nitrogen atom [46, 47]. It means that the hydrogen atom in the NH_2 and $NH(CH_3)$ groups forms less stable interactions than that formed by the methyl group in $N(CH_3)$, $N(CH_3)_2$, therefore the hydrogen bond in the liquid ammonia DN–H···N should be less stable than the specific interaction DN–CH_3←N. This reasoning permits considering the energies of the hydrogen bonds DN–H···N in the liquid ammonia and the formamide to be the same, equal 3.89 kJ mol^{-1}, and respectively the specific interactions N–CH_3←N in the liquid trimethylamine, *N*,*N*-dimethylformamide, and *N*-methylformamide equal 4.25 kJ mol^{-1}. The energy of the specific interaction DH–C=O→CH_3–N we take equal to the energy of this interaction in the liquid dimethyl ether (5.83 kJ mol^{-1}) (Chap. 3). Evidently, the electron density distribution in a molecule is governed by the properties of the atoms in its composition, therefore the substitution of the functional groups results in unequal changes in the energies of the intermolecular interactions formed by the bond vacancies of the molecule. Yet the above assumptions are valid for the estimation of the energies of the specific interactions in the complicated system of the functional solvents with a carbonyl oxygen connected through a carbon atom with a nitrogen atom securing a high negative charge (−0.368).

The mentioned types of the six hydrogen bonds existing in the liquid functional solvents (Fig. 2.12) and the specific interactions, whose energy and number constitute the vaporization enthalpy [15] make it possible to describe their contributions into this characteristic of the liquid *N*,*N*-dimethylformamide by the equation:

$$\begin{aligned}\Delta_{\mathrm{vap}}H^0\,(298) &= (2\mathrm{D{=}O}\cdots\mathrm{H{-}C{=}O} + 2\mathrm{D{=}O} \rightarrow \mathrm{CH_3\text{-}N}(5.83\times 2)\\ &\quad + 2\mathrm{DN\text{-}CH_3} \leftarrow \mathrm{N\text{-}CH_3}(8.40)) = 46.89\,\mathrm{kJ\,mol^{-1}}.\end{aligned}\tag{2.1}$$

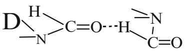
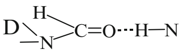
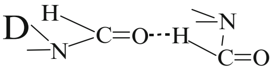
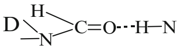
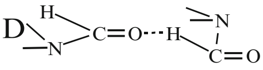
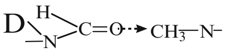
Subtracting the energy of the specific interactions DN–CH_3←N and D=O→ CH_3–N from the vaporization enthalpy we estimated the energy of the hydrogen bond $D = O\cdots H{-}C = O$ at 13.40 kJ mol^{-1} (Table 2.4).

Analogous equations describe the energy contributions of the hydrogen bonds and specific interactions in the *N*-methylformamide and the formamide, respectively:

$$\begin{aligned}\Delta_{\mathrm{vap}}H^0\,(298) &= 2\mathrm{D{=}O}\cdots\mathrm{H{-}C{=}O} + 2\mathrm{D{=}O}\cdots\mathrm{H{-}N{-}} + 2\mathrm{DN{-}CH_3}\\ &\quad \leftarrow \mathrm{N}(8.50) = 56.25\,\mathrm{kJ\,mol^{-1}}(\mathrm{NMF}),\end{aligned}\tag{2.2}$$

$$\begin{aligned}\Delta_{\mathrm{vap}}H^0\,(298) &= 2\mathrm{D{=}O}\cdots\mathrm{H{-}C{=}O} + 2\mathrm{D{=}O}\cdots\mathrm{H{-}N{-}}\\ &\quad + 2\mathrm{DN}\cdots\mathrm{H{-}N{-}}\,(7.78)\\ &= 64.98\,\mathrm{kJ\,mol^{-1}}(\mathrm{FA}).\end{aligned}\tag{2.3}$$

Table 2.4 Energies (kJ mol^{-1}) of hydrogen bonds and specific intermolecular interactions in liquid formamide, *N*-methylformamide, and *N*,*N*-dimethylformamide

Compound	$\Delta_{vap}H^0$ (298 K)	Energies of specific interactions		
FA	64.98	 D=O•••H-C 16.50	 D=O•••H-N 12.00	D–H–N···H–N– 3.90
NMF	56.25	 D=O•••H-C 13.40	 D=O•••H-N 10.55	D–N–CH_3←N 4.25
DMF	46.89	 D=O•••H-C 13.40	 D=O→CH_3-N 5.83	D–N–CH_3←N 4.25

The energies of the hydrogen bonds are as follows:

$$2D = O \cdots H\text{–}C = O + 2D = O \cdots H\text{–}N\text{–} = 47.75\ \mathrm{kJ\,mol^{-1}}(\mathrm{NMF}), \qquad (2.4)$$

$$2D = O \cdots H\text{–}C = O + 2D = O \cdots H\text{–}N\text{–} = 57.20\,\mathrm{kJ\,mol^{-1}}(\mathrm{FA}). \qquad (2.5)$$

The inequality (2.6) following from (2.1), (2.4), and (2.5) demonstrates the increasing energy contribution at replacing the specific interactions DH–C=O→CH$_3$–N in *N*,*N*-dimethylformamide by a more stable hydrogen bond 2DH–C=O$\cdots$H–N– in the *N*-methylformamide.

$$\begin{aligned}2D &= O \cdots H\text{–}C = O + 2D = O \cdots H\text{–}N\text{–}\,(57.15)(\mathrm{FA}) > 2D\\ &= O \cdots H\text{–}C = O + 2D = O \cdots H\text{–}N\text{–}\,(47.75)\cdot(\mathrm{NMF}) > 2D = O \cdots H\text{–}C\\ &= O + 2D = O \rightarrow CH_3\text{–}N\text{–}\,\left(38.49\,\mathrm{kJ\,mol^{-1}}\right)(\mathrm{DMF}).\end{aligned} \qquad (2.6)$$

Taking the energy of the hydrogen bond $D = O \cdots H - C = O$ equal to that in the liquid *N*, *N*-dimethylformamide (13.40 kJ mol^{-1}) we obtain the value of the energy of the H-bond $D = O \cdots H\text{–}N\text{–}$ equal 10.55 kJ mol^{-1}. The subsequent increase in the overall value of the energy corresponding to the same two types of the hydrogen bonds in the formamide shows their considerable stabilization taking into account the little difference in the hydrogen bond of low stability DN$\cdots$H–N– and the specific interactions DN–CH$_3$←N. The energy of these two types of hydrogen bonds may be estimated if, firstly, the energy of the hydrogen bond $D = O \cdots H\text{–}N\text{–} = 10.55\,\mathrm{kJ\,mol^{-1}}$ should be taken constant in the *N*-methylformamide and the formamide and, secondly, to take the energy of the hydrogen bond $D = O \cdots H\text{–}C = O = 13.40\,\mathrm{kJ\,mol^{-1}}$. The performed calculation of the energy of the hydrogen bond $D = O \cdots H\text{–}C = O$ resulted in the values 18.00 and 15.20 kJ mol^{-1}, respectively. The more realistic value of this type of hydrogen bond is the average value 16.50 kJ mol^{-1} and the value of the energy of the second type of hydrogen bond $D = O \cdots H\text{–}N\text{–}$ equal 12.00 kJ mol^{-1}. The estimated energies of these two types of hydrogen bonds form two regular series of stabilization:

$$\begin{aligned}D = O \cdots H\text{–}C = O(16.60)(\mathrm{FA}) > D = O \cdots H\text{–}C = O(13.40)(\mathrm{NMF})\\ \geq D = O \cdots H\text{–}C = O(13.40\,\mathrm{kJ\ mol^{-1}})(\mathrm{DMF}),\end{aligned} \qquad (2.7)$$

$$D = O \cdots H\text{–}N\text{–}\,(12.00)(\mathrm{FA}) > D = O \cdots H\text{–}N(10.50\,\mathrm{kJ\,mol^{-1}})(\mathrm{NMF}). \qquad (2.8)$$

Note that analogous series of the hydrogen bond stabilization in the liquid formamide, *N*-methylformamide, and *N*, *N*-dimethylformamide were suggested in [5] based on the investigation by the method of the RDF. The assumptions taken in the thermodynamic analysis of the energy of the hydrogen bonds and the specific interactions in the liquid functional solvents do not introduce considerable errors. This is confirmed by the energy of the hydrogen bonds in the liquid water (10.99 kJ mol^{-1}). On the contrary,

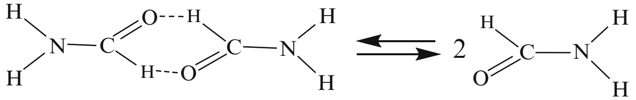


Fig. 2.13 Dissociation process of the dimer molecule of formamide in the vapor phase

the high energy of the hydrogen bond obtained by the quantum-chemical calculations [5] for the chain (67.8 kJ mol^{-1}) and ring (63.2 kJ mol^{-1}) structure of the liquid formamide in comparison with the vaporization enthalpy (64.98 kJ mol^{-1}) does not exclude the presence in vapor of dimeric molecules.

The trend in the decrease of the hydrogen bond energy in the series of formamide derivatives differing 1.5 times at the extremes of this series make it possible also to suggest the presence of dimers in the vapor of the formamide and the absence of dimers in the vapor of its derivatives.

$$\begin{aligned} &D = O\cdots H\text{–}C = O(16.50)(FA) > D = O\cdots H\text{–}C = O(13.40)(NMF) \\ &\quad\approx D = O\cdots H\text{–}C = O(13.40)(DMF) > D \\ &\quad = O\cdots H\text{–}N(12.00)(FF) > D = O\ldots H\text{–}N\ (10.55\,kJ\,mol^{-1})(NMF). \end{aligned} \tag{2.9}$$

The energy of the hydrogen bonds of the liquid formamide does not fundamentally contradict to the presence of dimers in its vapor since the reduction to two of the number of coordinated molecules and the decrease in the number of the intermolecular interactions from six to two in the dimer secures the stabilization of the hydrogen bonds (Fig. 2.13). The fulfillment of these conditions is necessary for the dimerization in the vapor as is observed at the analogous relation between the vaporization enthalpy and dissociation energy of the triethylaluminum dimer [20, 21].

2.4 Energy of Specific Interactions in Liquid Acetonitrile and Dimethyl Sulfoxide

The acetonitrile does not form hydrogen bonds [5, 32, 48–51] and in the nearest surrounding in the liquid state are situated two molecules oppositely directed [5, 51]. This pattern is an unjustified simplification of the structure of the liquid acetonitrile suggesting the formation of weakly bound dimers of low stability having the vaporization enthalpy of 32.7 kJ mol^{-1}. This concept [5, 51] does not provide an understanding of the specificity of its intermolecular interactions in the liquid state. Therefore, applying this concept we have suggested that the acetonitrile molecule has two bond vacancies originating from the unshared electron pair of the nitrogen and from the essentially unshared $2s^2$-electron pair on the carbon atom of the methyl group (Fig. 2.14), forming as a result chain and ring structures in the liquid acetonitrile (Fig. 2.14a, b). Consequently, the acetonitrile molecule has two specific

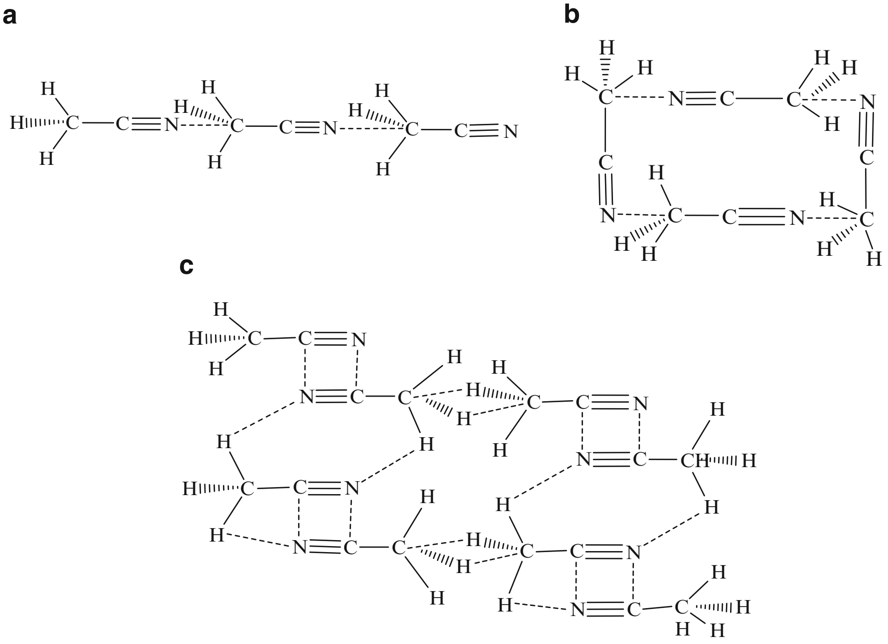


Fig. 2.14 Schematic picture of the liquid structure of acetonitrile (**a**) chain, (**b**) ring (carbon atom of the fragment –C ≡ N does not take part in the intermolecular interaction), and (**c**) network-chain structure

interactions –C–H_3C←N≡C–, whose energies equal D–C–H_3C←N≡C– = $\Delta_{vap}H^0$ (298 K)/2 = 32.7/2 = 16.35 kJ mol^{-1}. The energy of this type of specific interactions is approximately four times larger than the energy of the interaction DN–CH_3←N– (4.20 kJ mol^{-1}) existing in the liquid trimethylamine, and they are 1.5-fold more stable than the hydrogen bonds in water.

It is more realistic to assume that the more stable specific interactions are formed by the unshared electron pair of the nitrogen and by the essentially unshared $2s^2$-electron pair of the carbon atom with a triple bond. The remaining bond vacancy of the carbon atom from the methyl group forms an interaction with the hydrogen of the methyl group H_3C→H–CH_2 of the contiguous molecule (Fig. 2.14c) analogously to methanol [38, 40] (Chap. 1). The RDF of the acetonitrile [5] is well consistent with the schematic picture of its liquid state shown in Fig. 2.14. Thus, the acetonitrile molecule with four bond vacancies forms two interactions –C≡N→C≡N of high stability and two specific interactions DH_3C→H–CH_2 of low stability with the estimated energy of 0.60 kJ mol^{-1} (Chaps. 1 and 3). The energy of the specific interactions D–C≡N→C≡N is estimated from the difference between the vaporization enthalpy and the overall energy contribution of the interactions of low stability (2.10):

$$\mathrm{DC \equiv N \rightarrow C \equiv N} = \frac{\Delta_{\mathrm{vap}}H^0\,(298) - \mathrm{DH_3C \rightarrow H - CH_2}}{2}. \tag{2.10}$$

The high energy of this type of specific interactions (15.75 kJ mol^{-1}) indicates the large difference of the charges on the carbon and nitrogen atoms due to the shift of the electron density in the triple bond of acetonitrile.

The thorough investigation by the diffraction method of the solutions of acetonitrile and *N*,*N*-dimethylformamide in 1:1 ratio showed that the molecules are antiparallel oriented [5, 51] with a short distance between the molecules of acetonitrile and *N*,*N*-dimethylformamide (316 pm), while the distance between the acetonitrile molecules in the liquid state is 330 pm. Therefore, it is presumable that the existing in the solution specific interactions $=\mathrm{O}\rightarrow\mathrm{CH_3}$–C–N; –N–$(\mathrm{H_3})$C←N–; –C–$(\mathrm{H_3})$C←N–C– are more stable than the interactions in the liquid initial compounds, and the following inequality is valid (2.11):

$$\begin{aligned}\mathrm{D{=}O \rightarrow CH_3{-}C{-}N > D{-}C{-}H_3C \leftarrow N \equiv C\text{-}}\ \left(15.75\,\mathrm{kJ\,mol^{-1}}\right)\\ (\mathrm{AN}) > \mathrm{D{=}O \cdots H{-}C{=}O}\ \left(13.5\,\mathrm{kJ\ mol^{-1}}\right)(\mathrm{DMF}).\end{aligned} \tag{2.11}$$

The negative value of the mixing enthalpy (-200 kJ mol^{-1}) for the solutions in 1:1 ratio [52] confirms the higher stability of the specific interactions in the solution than in the liquid acetonitrile and *N*,*N*-dimethylformamide.

The dimethyl sulfoxide has a structure of a trigonal pyramid. The carbon and oxygen atoms are located in the plane of the pyramid base which should be distorted. The electron density distribution in the molecule (Fig. 2.15) [5, 53] results in a high positive charge on the sulfur atom (0.212), a negative charge on the oxygen atom (-0.281), and a significantly lesser negative charge on the carbon atoms of the methyl groups (-0.096). The dimethyl sulfoxide molecule has four bond vacancies, two due to the oxygen atom, and two, from the essentially unshared $2s^2$-electron pairs of the carbon atoms of the methyl groups. Four specific interactions of the same type D–S=O→$\mathrm{CH_3}$–S= are formed. The radial distribution curve for dimethyl sulfoxide contains two peaks at 400–700 pm [5] less pronounced than the analogous peaks of the formamide (350–550 pm). These data allow to suppose, that the dimethyl sulfoxide forms a hydrogen bond more stable than the formed specific interactions and which has insignificant distinction from the hydrogen bond in the liquid *N*,*N*-dimethylformamide. Four bond vacancies of the dimethyl sulfoxide take part in the interactions in the liquid state with two molecules of the nearest surrounding and in the formation of the chain structure of the liquid state (Fig. 2.16) involving specific interactions D–S=O→$\mathrm{CH_3}$–S= whose energies are determined from the vaporization enthalpy $\Delta_{\mathrm{vap}}H^0$ (298 K) = 52.88/4 = 13.22 kJ mol^{-1}.

The energy of this type of specific interactions has the insignificantly decreased value compared with the energy of the hydrogen bonds D=O···H–C=O (13.40 kJ mol^{-1}) in the *N*-methylformamide and *N*,*N*-dimethylformamide and the essentially reduced value compared to that of the hydrogen bond energy of the

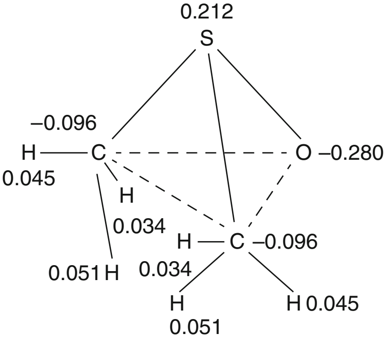


Fig. 2.15 Structure and charge distribution in molecule of dimethyl sulfoxide

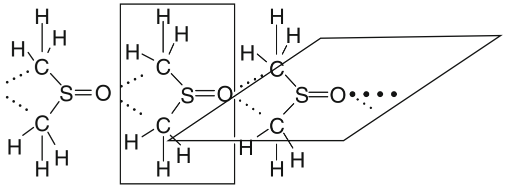


Fig. 2.16 Schematic picture of the liquid structure of dimethyl sulfoxide

formamide (16.60 kJ mol^{-1}). This succession in the energy value of the hydrogen bonds D=O···H–C=O and of the specific interaction D–S=O→CH$_3$–S= in the dimethyl sulfoxide is in complete agreement with the conclusions from the radial distribution curves.

2.5 Hydrogen Bonds and Specific Interactions of *N*,*N*-Dimethylformamide in Solvents

The conclusions on the six-coordination state of the *N*,*N*-dimethylformamide, *N*-methylformamide, and formamide can be supplemented with the data [52] on the complex formation with various solvents. In this connection, we shall discuss the influence of the composition of the binary system *N*,*N*-dimethylformamide–phosphoric acid on the dynamic viscosity of the system [54]. Note that there is no correct equation describing the viscosity of the ideal solutions proceeding from the properties of the individual components. The existing semiempirical equations describing the viscosity isotherms of certain systems are quite unsuitable for the description of the other systems. The concept of the positive deviation on the isotherms of viscosity and isotherms of excessive viscosity is generally recognized. The positive deviation from the additivity is commonly ascribed to the formation in solutions of more stable interactions than in the initial compounds [54]. The experimental data of [54] on the viscosity of solutions in the system *N*,*N*-dimethylformamide–phosphoric acid measured with the accuracy up to 1% show the positive deviation in the total range of the compositions (Fig. 2.17).

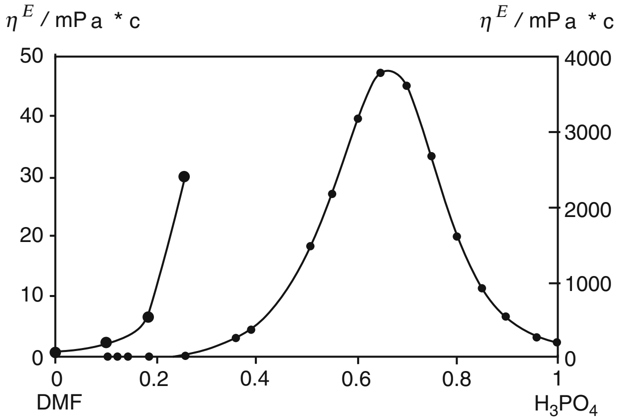


Fig. 2.17 Dependence of the isotherm (298 K) of dynamic viscosity (η/mPa s) on concentration of solution in system *N*,*N*-dimethylformamide–H_3PO_4: curves (1) (0–25) and (2) (0–100 mol% H_3PO_4) are shown in different scale

This character of viscosity variation with the solution composition is conserved in the temperature range 298–338 K where the viscosity decreases 12-fold.

The maximum on the isotherm in question at 66.7 mol% H_3PO_4 indicates the formation of a complex of the composition $(H_3PO_4)_2$·DMF [54–56] between the phosphoric acid dimer and the *N*,*N*-dimethylformamide. The dimers of the acid exist in the water solutions, and their presence in the *N*,*N*-dimethylformamide was substantiated in [57]. The excessive molar viscosity of solutions (η_M^E) in this system repeats the character of the dependence of the dynamic viscosity (η^E) confirming the formation of a stable complex in the solution [54]. According to Fadeeva et al. [58, 59] the narrowness of the peak and the form of the maximum on the curve viscosity–concentration correspond to the stability of the complex formed in the solution [58, 59]. In the discussed case, the maximum illustrates the high stability and consequently the low dissociation degree. In this connection, the primary viscosity growth at dissolution of the phosphoric acid in DMF in the range 0–25 mol% of H_3PO_4 (Fig. 2.18) changed by steep increase in the viscosity from 30 to 260 (η/mPa s) at the content of the phosphoric acid 26.5 mol% shows the finished process of the destruction of the structure of liquid DMF and the end of the formation of the solvate of the composition 3:1 = DMF:H_3PO_4 with coordinating center on the phosphoric acid molecule. This means that the dimers of the phosphoric acid completely dissociated in the solvent and formed a solvate structure of relatively low viscosity about 20 times greater than that of the *N*, *N*-dimethylformamide. It is therefore presumable that the specific intermolecular interactions formed in the solvate are hardly different in the stability from the interactions existing in liquid DMF. The low values of the dynamic viscosity of solutions in the composition range 0–25 mol% of H_3PO_4 and the positive deviation on the viscosity isotherms show that the energy of dissociation of the phosphoric acid dimers is partially or completely compensated by the newly formed specific interactions.

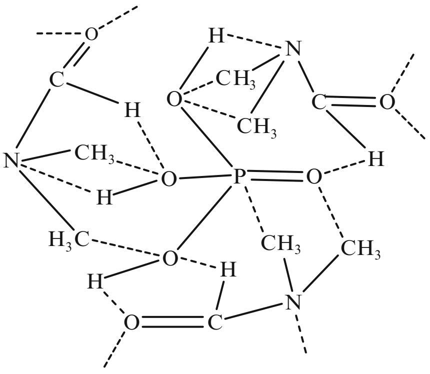
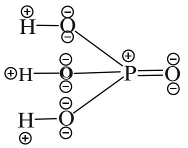


Fig. 2.18 Schematic picture of a complex of *N*,*N*-dimethylformamide with phosphoric acid

The molecule of the phosphoric acid with 12 bond vacancies is capable to coordinate in the nearest surrounding two and more molecules of *N*,*N*-dimethylformamide.



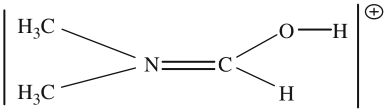
However, the presence in the near surrounding of three DMF molecules is preferable since each molecule having six bond vacancies forms a solvate of the 3:1 composition and with the remaining two bond vacancies cross-links them into the network structure of the solution (Fig. 2.18). Further increase in the phosphoric acid content results in the 25-fold increase in the dynamic viscosity of the solution, approximately from 29 to 3,800 (η/mPa s) ensuring the complex formation, and then the subsequent increase in the phosphoric acid concentration leads to the decrease in the dynamic viscosity finally to the value characteristic of the pure acid.

The growing viscosity in solutions with the concentration of the phosphoric acid in the range 25–66.7 mol%, occurs, on the one hand, because of the destruction of the solvate structure with the molecule of the phosphoric acid as the coordination center, and on the other hand, due to the processes at the enhanced concentration of the phosphoric acid increasing the viscosity of the solution. The understanding of these processes can be provided by the spectral investigations [59] of liquid DMF, phosphoric acid, and their solutions.

According to Corbridge [60] the 100% phosphoric acid undergoes autoprotolysis:

$$2\mathrm{H_3PO_4} = \mathrm{H_4PO_3^+} + \mathrm{H_2PO_4^-}.$$

However, this process in the DMF solution is hampered by the formation of the specific intermolecular interactions between the molecules of the solvent and the solute. The spectral study of the phosphoric acid dissolution in diphenylamine showed that at the primary dissolution the intensity ratio of the main absorption bands of the components changed, and a strong background absorption was observed [55] indicating the formation of the specific intermolecular interactions between the components. This means that the protonation of the phosphoric acid did not occur. However, even at the initial dissolution of the phosphoric acid in DMF in the spectrum of the DMF solution a band of the stretching vibrations P–O–P (889 cm^{-1}) is observed whose position remains virtually unchanged at the increasing concentration of the phosphoric acid. The presence of this band shows that even at the low concentration of H_3PO_4 the dehydrated form of the phosphoric acid is present in the solution [6, 55, 60]. At the same time in the solutions of this system, the overlapping occurs of the bands of the stretching vibrations of groups P=O (1,145 cm^{-1}) of the phosphoric acid and the bending vibrations of the group N–C–H (1,092 cm^{-1}) of DMF molecules which in its turn should be assigned to the formation of the specific intermolecular interactions between the molecules of DMF and phosphoric acid. In the spectra of solutions in the range of phosphoric acid content 0.0–0.7 mol fractions, the band of the stretching vibrations of the C–N bond (1,387 cm^{-1}) of the DMF molecule appears and shifts (7 cm^{-1}) to the low frequency region with the simultaneous decrease in its intensity. These data show the stabilization of the bond presumably due to the interactions of the free bond vacancy of the nitrogen atom with the hydrogen atoms of the phosphoric acid providing a hydrogen bond of low stability with the energy similar to that of the hydrogen bond in the liquid ammonia. After reaching the maximum on the plot of the dynamic viscosity of the solution versus its composition (Fig. 2.17) at 0.7 mol fraction of H_3PO_4, the band of the stretching vibrations of the C–N bond (1,387 cm^{-1}) of the DMF molecule disappears and lacks in the region of the compositions 0.7–1.0 mol fraction of the acid. At the same time at the initial addition of the acid and the subsequent increase in its concentration, the low-frequency wing of the stretching vibration band of the C=O bond (1,674 cm^{-1}) of DMF suffers widening and the shift to the low frequency side. This suggests that the free bond vacancies of the carbonyl oxygen form specific intermolecular interactions of low stability. At the acid content of 0.7 mol fraction a band at 1,709 cm^{-1} appears lacking at lower concentration of the acid and characteristic of the stretching vibration of the C=N bond in the protonated DMF [61].



Consequently, a steep decrease occurs in the dynamic viscosity of the solution in the range 0.7–1.0 mol fraction of the acid due to the protolytic reaction and general decrease in the H_3PO_4 concentration (Fig. 2.17). It should also be noted that at reaching 0.2 mol fraction of the phosphoric acid in the solution the intensity of the band of the bending vibrations of the group O=C–N (658 cm^{-1}) of the DMF molecule sharply decreases, and in the DMF spectrum appears a strong band at 672 cm^{-1} which should be assigned to the formation by this group of the specific interactions in the solvate structure. Just in this region the destruction of the structure of liquid DMF is finished, and the solution acquires the solvate structure (Fig. 2.18) with the components ratio 3:1. Further a structure begins to form where the coordinating center is the DMF molecule, but with the growing acid concentration gradually the DMF protonation occurs. At the H_3PO_4 concentration of 0.7 mol fraction, the band at 672 cm^{-1} also disappears confirming the existence of the DMF in the protonated form. Therefore, the high dynamic viscosity of solutions beginning from 40 to 50 mol% of the acid is due to the involvement into the interactions of $H_4P_2O_7$, deprotonated forms of the acid, and the protonated forms of DMF accompanied with the formation of a complex with stable hydrogen bonds.

The dependence of the dynamic viscosity on the concentration shown in Fig. 2.17 has the same character for the phosphoric acid solutions in water and in organic solvents butyl formate, formamide, diisopropyl ether. The solutions of these systems are characterized by the position of the maximum deviation from the additivity of the viscosity curve in the range of the phosphoric acid concentration 0.6–0.7 mol fraction. The height of the maximum peak decreases in the series [61, 62]:

$$\text{DMF}[62] > \text{Diisopropyl ether} > \text{Formamide} > \text{Butylformate} > \text{water}[63]. \quad (2.12)$$

The existing correlation between the height of the maximum and the complex stability indicates the decrease of the hydrogen bonds stability in this series. Therefore, we are able to conclude that the six-coordinate state in the solutions under consideration is due to the bond vacancies of oxygen atom and the hydrogen atom linked to the carbonyl group, to the same oxygen atom and the carbon atom of the methyl group, to the nitrogen atom and the carbon atom of the methyl group, or the hydrogen atom of the amino group, respectively.

The results of the realized untraditional approach to the thermodynamic analysis and the established laws of the variation in the energy of the hydrogen bonds and the specific interactions in the liquid acetonitrile, dimethyl sulfoxide, *N*,*N*-dimethylformamide, *N*-methylformamide, and formamide illustrate the validity of this approach and the adequate interpretation of the interactions nature. Thus, the well-grounded rejection of the model of the sp^3-hybridization allowed for the first time the application of the concepts of the theoretical chemistry to the understanding of various types of specific interactions and hydrogen bonds in organic compounds and to the estimation of their energies.

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