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THE SEMIEMPIRICAL QUANTUM CHEMICAL STUDIES OF SOME PROPERTIES OF CLUSTERS FORMED IN FORMAMIDE–1-PROPANOL MIXTURES

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The optimization of the geometry and characteristics of the hydrogen bonds in clusters formed by molecules in the formamide (F)–1-propanol (PrOH) mixtures by means of the semiempirical quantum chemical method (MOPAC 6.0) have been carried out.

Net charge distribution in trimers (2F·PrOH) and pentamers (3F·2PrOH) allowed to explain the deviations from ideality of dielectric permittivity in F–PrOH mixtures.

KEY WORDS: quantum chemistry, hydrogen bond, binary liquid mixtures.

INTRODUCTION

This work is a continuation of our earlier studies on the analysis of intermolecular interactions in the liquid binary mixtures of formamide with different alcohols¹.

In our previous paper¹, using the ¹H-NMR examinations of liquid formamide (F)–1-propanol (PrOH) binary mixtures and changes in the main physicochemical properties of these mixtures (density, viscosity, dielectric permittivity) as well as their deviations from “ideality”, an analysis of the intermolecular interactions have been

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carried out. The chemical shift differences $\delta(\text{F-PrOH})$ were measured, at 298 K, between the center of the $^1\text{H-NMR}$ signal of formyl proton of F molecules and the center of $^1\text{H-NMR}$ signal of $-\text{OH}$ group of PrOH molecules over the wide range of solvent composition. Subsequently from these new spectral data the structural spectral parameters $\Delta\delta(\text{F-PrOH})$ have been evaluated. The changes of spectral parameters $\Delta\delta$ exhibit maximum at ca. 60 mol. % of F. Thus, the conclusion would be drawn that at this composition the strongest interactions between F and PrOH molecules with involving hydrogen bonds, are displayed and the most stable "complex" (sub-unit) is of the $3\text{F}\cdot 2\text{PrOH}$ type. We have also calculated the values of temperature coefficient of dielectric permittivity (α_{12}), viz. $\alpha_{12} = (1/\epsilon_{12}) \cdot [d\epsilon_{12}/d(1/T)]$. It has been shown in our previous paper^{1,2} that there is a full consistence of conclusion drawn from the analysis of changes in spectral parameters $\Delta\delta$ and coefficient α_{12} . The temperature coefficient of dielectric permittivity attains the highest value within the composition range corresponding to about 60 mol.% of F. This would correspond to the formation of the stable "complex" (sub-unit) of $3\text{F}\cdot 2\text{PrOH}$ type, which has been confirmed by the spectral $^1\text{H-NMR}$ measurements.

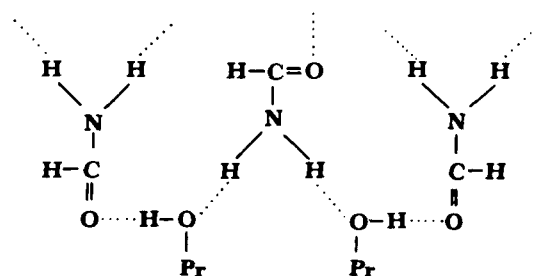
As has been shown in our previous paper^{1,2}, additional information about intermolecular interactions in liquid binary mixtures is provided by the analysis of deviations from "ideality" of basic physicochemical properties of these mixtures, i.e., density, viscosity, dielectric permittivity and calculated from these data molar volumes and kinematic viscosities. In the F-PrOH mixtures the deviations from "ideality" of density, viscosity, molar volume and kinematic viscosity attain the highest values at the F content amounting to about 60 mol.%. Thus the F-PrOH mixtures with this composition should be treated as "dense and viscous to maximum". This effect can be accounted for by the increase in the number of hydrogen bonds formed between F and PrOH molecules, which consequently leads to the formation of stable intermolecular "complexes" of the $3\text{F}\cdot 2\text{PrOH}$ type. The changes in deviations from "ideality" of dielectric permittivity attain the extreme value at about 70 mol. % of F, which most likely point to the formation of $2\text{F}\cdot\text{PrOH}$ "complexes" in liquid mixtures of formamide and 1-propanol. Assumed structures of the "complexes" of the $3\text{F}\cdot 2\text{PrOH}$ and $2\text{F}\cdot\text{PrOH}$ types are shown in Figure 1.

Previously¹, we were not able to estimate the strength of hydrogen bonds formed between molecules of formamide and 1-propanol in case of the structures of "complexes" of $3\text{F}\cdot 2\text{PrOH}$ and $2\text{F}\cdot\text{PrOH}$ types.

Therefore in the present work we have attempted to solve this problem using quantum chemical calculations.

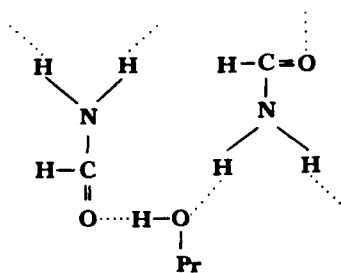
RESULTS AND DISCUSSION

The hydrogen bonds presumably act as "stabilizing bridges" between the formamide (F) and 1-propanol (PrOH) molecules in $3\text{F}\cdot 2\text{PrOH}$ (pentamer) and $2\text{F}\cdot\text{PrOH}$ (trimer) clusters occurring, as it was mentioned above, in the F-PrOH mixtures. Since the valence electrons in these molecules should play the most important role



3F·2PrOH

(sub - unit)



2F·PrOH

(sub - unit)

Figure 1 The proposed stable "complexes" occurring in the formamide-1-propanol mixtures.

in the hydrogen bonds creation, the use of one of the semiempirical quantum-chemical methods may be sufficient to evaluate the binding energy, charge transfer and bonds lengths of hydrogen bonds as well as the total geometry of clusters.

In this paper the MOPAC 6.0 Package Program³ has been used for the cluster geometry optimization. This new version of MOPAC, described thoroughly in 1990 by Stewart⁴, includes the significant improvements in comparison to the older version of this program. One of the most important advantages relies on the introduction to this version the so-called MNDO-PM3 parametrization (the Modified Neglect of the Diatomic Overlap, Parametric Method Number 3)⁵. In the MNDO and AM1 (Austin Model 1)⁶ of previous versions of MOPAC the intra- and intermolecular integrals, needed for calculations, have been parametrized by means of the experimental values for isolated atoms. In the PM3 one-center two-electron integrals were optimized to reproduce well experimental molecular properties.

In majority of cases, as it was shown by Stewart⁴, the PM3 parametrization significantly reduces the discrepancies between calculated and measured values of

the several important physicochemical parameters such as: the heat of formation (ΔH_f), the dipole moment (μ), the bond length (r) as well as planar and dihedral angles.

So the MOPAC 6.0 offers the possibility of selection of the AM1 or PM3 hamiltonians, working much better with organic clusters than MNDO hamiltonian, to be used for calculation of the values mentioned above and comparison with experimental data if available.

As the first step of calculation the heats of formation and dipole moments of the fully optimized formamide and 1-propanol single molecules have been computed by means of the AM1 and PM3 and compared with measured results in order to choose a proper semiempirical method for further cluster calculations. The following values were obtained:

$$(\Delta H_f)_F^{\text{AM1}} = -44.756 \text{ kcal/mole}; \quad (\Delta H_f)_F^{\text{exp}} = -44.50 \text{ kcal/mole}^4$$

$$(\Delta H_f)_F^{\text{PM3}} = -41.824 \text{ kcal/mole}$$

$$(\Delta H_f)_{\text{PrOH}}^{\text{AM1}} = -69.532 \text{ kcal/mole}; \quad (\Delta H_f)_{\text{PrOH}}^{\text{exp}} = -62.30 \text{ kcal/mole}^7$$

$$(\Delta H_f)_{\text{PrOH}}^{\text{PM3}} = -62.200 \text{ kcal/mole}$$

$$\mu_F^{\text{AM1}} = 3.698 \text{ D}; \quad \mu_F^{\text{exp}} = 3.730 \text{ D}^4$$

$$\mu_F^{\text{PM3}} = 3.113 \text{ D}$$

$$\mu_{\text{PrOH}}^{\text{AM1}} = 1.537 \text{ D}; \quad \mu_{\text{PrOH}}^{\text{exp}} = 1.657 \text{ D}^7$$

$$\mu_{\text{PrOH}}^{\text{PM3}} = 1.425 \text{ D}$$

It seems worth mentioning that all MOPAC's versions apply the same general approach to the optimization of the molecules or cluster's geometry. Using the derivatives of the energy with respect to coordinates the bond lengths as well as planar and dihedral angles are changed so as to lower the heat of formation. When no further change can significantly lower the heat of formation the optimization is stopped. The geometry of molecules corresponds then to the stationary point on the potential surface⁴.

The AM1 method has been selected for cluster calculations. Considering results for single molecules discussed above the only significant difference occurs in a case of the heat of formation of 1-propanol molecule for AM1 hamiltonian. In contrary the discrepancies of heats of formation $(\Delta H_f)_F^{\text{PM3}}$ and dipole moments μ_F^{PM3} and $\mu_{\text{PrOH}}^{\text{PM3}}$ are larger than for the AM1.

The geometrical parameters optimized by the AM1 method for formamide and 1-propanol molecules are given below:

1° for F molecule—the bond lengths given below (in brackets experimental values according to⁴) are equal to: CH = 1.114 Å (1.102 Å), CO = 1.243 Å (1.193 Å)

CN = 1.369 Å (1.376 Å), NH = 0.989 Å (1.002 Å); the planar angle OCN = 123.1° (123.8°); the dihedral angles HNCO = ± 179.97°.

2° for PrOH molecule—the bond lengths are equal to: CC = 1.51 Å, CO = 1.42 Å, OH = 0.963 Å, CH = 1.12 Å; the planar angles CCC = 110.82°, CCO = 107.12°, COH = 106.57°, HCC = 109.73°; the dihedral angles OCCC = + 179.96°, HOCC = - 179.52°, HCCC = ± 58.37°, HCCC (hydrogen from a methyl group) = 179.94°.

In the second step of calculation the 3F·2PrOH and 2F·PrOH clusters shown in Figure 1, respectively as pentamer and trimer have been considered as stable “complexes”. In this case the optimized geometries of separate molecules were kept frozen and only intermolecular distances and planar as well as dihedral angles have been optimized.

The images of the studied clusters are shown in Figures 2 and 3. In these Figures the hydrogen bonds of the O.....H type have been marked by means of dashed lines. There are six and three hydrogen bonds in pentamer and trimer, respectively.

Two main criteria as the hydrogen bond existence in a cluster have been taken into account⁸:

1° a significant charge transfer between two neighbouring atoms (O.....H) in cluster with respect to the charge on the atoms in the free molecules;

2° bond length was chosen as the shortest of all theretically possible hydrogen bonds.

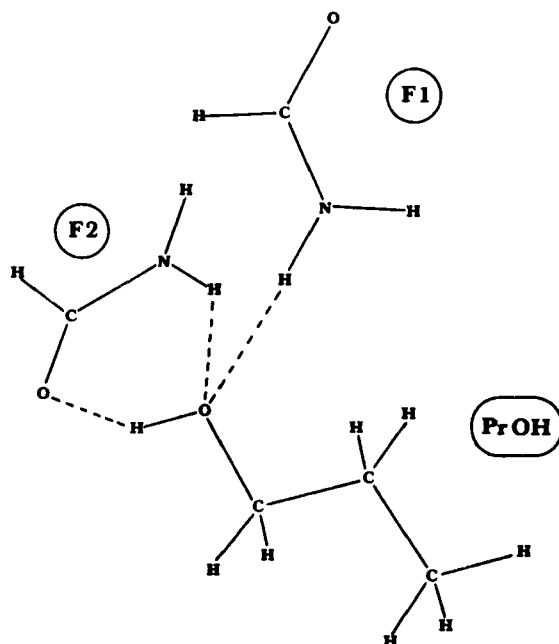


Figure 2 Geometrical structure of the 2F·PrOH trimer optimized by the AM1 method.

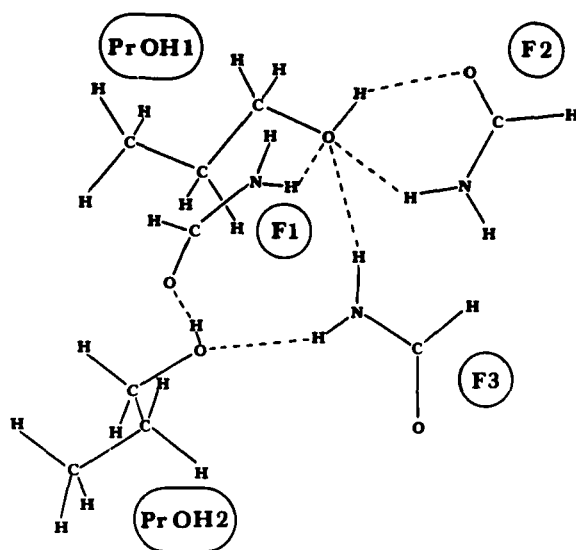


Figure 3 Geometrical structure of the 3F·2PrOH pentamer optimized by the AM1 method.

Table 1 Characteristics of the hydrogen bonds and the net charges in 2F·PrOH and 3F·2PrOH clusters calculated by means of the AM1

<i>A kind of cluster</i>	<i>The number of hydrogen bonds</i>	ΔE^H per one hydrogen bond [kJ/mole]	<i>Average bond length [Å]</i>	<i>Net charges on molecules in clusters [in e]</i>
2F·PrOH (Trimer)	3	-13.07	2.16	$\Delta_{q_{F1}} = -0.0037$ $\Delta_{q_{F2}} = +0.0038$ $\Delta_{q_{PrOH}} = -0.0001$
3F·2PrOH (Pentamer)	6	-11.57	2.17	$\Delta_{q_{F1}} = -0.0054$ $\Delta_{q_{F2}} = +0.0037$ $\Delta_{q_{F3}} = +0.0002$ $\Delta_{q_{PrOH(1)}} = +0.0026$ $\Delta_{q_{PrOH(2)}} = -0.0009$

In accordance with the previously published results^{8,9} the hydrogen bond length can change in clusters from 1.25 Å for F⁻.....H bond in thiourea trimers TU – F⁻ – TU⁸ up to 2.31 Å for O.....H in nitromethane thiourea trimers NM – TU – NM⁹.

In Table 1 the main properties of the hydrogen bonds occurring in 3F·2PrOH and 2F·PrOH clusters have been collected.

The interaction energy (ΔE^H), recalculated per one hydrogen bond, was determined from the given below equations:

$$\Delta E^H = E_{3F \cdot 2PrOH}^{AM1} - (3E_F^{AM1} + 2E_{PrOH}^{AM1}) \quad \text{and} \quad \Delta E^H = E_{2F \cdot PrOH}^{AM1} - (2E_F^{AM1} + E_{PrOH}^{AM1})$$

for pentamer and trimer, respectively. This energy can be regarded as hydrogen bond strength. As we can see its value is approximately the same for pentamer (-11.57 kJ/mole) and trimer (-13.07 kJ/mole). It points to rather weak hydrogen bonds formed in the formamide-1-propanol solutions in respect to other systems^{8,9}. The highest hydrogen bond strength was obtained in thiourea clusters containing F^- and NO_3^- ions: $\Delta E^H = -276.27$ kJ/mole and -113.22 kJ/mole for $TU-F^-TU$ and $TU-NO_3^- - TU$ trimers, respectively⁸. The lowest strength occurred in thiourea-nitromethane system, i.e., $\Delta E^H = -9.93$ kJ/mole for $NM-TU-NM$ cluster⁹. So the energies shown in Table 1 are of an order comparable with the last mentioned above.

In the last column of Table 1 the total net charge distribution on molecules entering into the composition of trimer $2F \cdot PrOH$ and pentamer $3F \cdot 2PrOH$ has been displayed. It is evident that in the case of trimer the cluster treated as a whole reveals the properties of a dipole with the negative and positive poles on the formamide molecules and with neutral 1-propanol molecule. This fact is of a great importance for the explanation of an existence of dielectric permittivity maximum attained at about 70 mol. % of the formamide in $F-PrOH$ solutions.

It is known¹⁰ that dielectric permittivity ϵ can be calculated for the system placed in the electric field from the equation: $\epsilon = \sigma/(\sigma - \bar{\mu})$, where σ stands for the charge of the electric field and $\bar{\mu}$ is an average dipole moment generated by a field and recalculated by unit volume of the system considered.

So in the case of the $2F \cdot PrOH$ trimers formed in solution at about 70 mol. % of F , an average dipole moment μ following from the net charge distribution should increase the value of dielectric permittivity as it is observed experimentally. For the $3F \cdot 2PrOH$ pentamer the distribution of the net charge in a cluster is more complex, without distinct poles, and an average moment should be lower than previously. For this reason the pentamer does not influence on the dielectric permittivity maximum.

It seems to be relevant to emphasize here that an average dipole moment μ considered above can differ significantly from a normal dipole moment μ of the cluster since it includes also the "image" moment generated in a cluster by electric field.

However, the value of this generated moment should be proportional to the initial negative and positive poles occurring in cluster without any field.

CONCLUSIONS

In the present paper the properties of clusters treated as the stable "complexes" (sub-units) in the formamide-1-propanol solutions formed at about 60 and 70 mol. % of formamide have been analysed by means of the semiempirical quantum chemical MOPAC 6.0 Package.

It follows from these quantum chemical calculations that the properties of clusters consisting of pentamers ($3F \cdot 2PrOH$) and trimers ($2F \cdot PrOH$) are presumably responsible for occurring the deviations from "ideality" of the density, viscosity, molar volume, kinematic viscosity and dielectric permittivity in the $F-PrOH$ mixtures.

It particular, the net charge distributions in trimers and pentamers allow us to explain the deviation from "ideality" of the dielectric permittivity at about 70 mol. % of formamide.

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