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Spectra and structure of binary azeotropes VI-benzene-methanol

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1. Introduction

Infrared and ¹H NMR spectroscopy are powerful methods for the study of intermolecular forces between different molecules such as mixture of solutions. Most of characteristic effects observed are the frequency shift and chemical shift due to hydrogen bonding. $\Delta \upsilon$ (cm⁻¹) defined as a difference in position between a free stretching and deformation vibrational band in pure substance and bonded counterpart displaced to lower and higher frequencies, respectively. $\Delta\delta$ (ppm) defined as a difference in position between a shielded or deshielded proton in new environment. We therefore set out to obtain direct structural information about benzene–methanol azeotrope using spectroscopy, in the hope of obtaining evidence for the unit-structure of this constant boiling mixture.

The accent in this work is therefore on *structure*: obviously, structure and dynamics are intimately linked in fluid systems, as is nicely illustrated by the fact that, while infrared spectroscopy'sees' a largely static system, very much on the slow-exchange side, NMR spectroscopy detects a largely dynamic system, almost always on the fast-exchange side.

The FT-IR and ¹H NMR spectra of pure liquids and azeotrope contains information on intermolecular forces and unit-structure of the cluster frequency and environment domain spectroscopic methods like FT-IR, FT-Raman, and ¹H NMR are well studied for this work.

ABSTRACT

Benzene and methanol make a minimum boiling point homogeneous binary azeotrope with the mole ratio 2:3. Some characteristic vibrational modes, as well as ¹H NMR signals change due to the azeotrope formation. The extend of interaction of these molecules causes significant changes on some vibrational modes involved, and ¹H NMR signals show some changes on their position. No IR, Raman, and NMR spectra have been reported for this constant boiling mixture, also there has not been any attempt to investigate the unit-structure of this azeotrope. In this work the FTIR, FT-Raman, and ¹H NMR spectra of pure benzene, pure methanol, and corresponding azeotrope were recorded, mutual influences resulting from azeotrope formation have been analyzed, and spectral changes has been discussed. The unit-structure of cluster has been deduced based on mole ratio, boiling point depression of constituents, and comparison among the spectra obtained by FTIR, FT-Raman, and ¹H NMR techniques.

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Among all investigations done about benzene–methanol mixtures and/or their azeotrope, there has not been any explicit attempt to determine unit-structure of this azeotrope and its IR, Raman, and NMR spectra. Considering methanol alone, there have been various theoretical and experimental efforts describing the hydrogen bond strength and its structure [1–7]. Also, various spectroscopic techniques, such as Raman, X-ray, and neutron scattering have been used to study this system [4–6]. NMR has also established itself as a method of probing the dynamics and structure of methanol liquid [8–11]. It is well known that methanol molecules interact through hydrogen bonds similar to those between water molecules. The details of these interactions are important in determining the configurations of small groups of molecules and eventually the structure of the liquid and solid phases of methanol.

Experimentally, several methods have been used to study interactions between methanol molecules. A number of PVT and heat capacity measurements on methanol vapor have been reported [12–14]. In this regard Weltner and Pitzer [12] suggest the presence of monomers, dimmers, and tetramers from PVT and heat capacity data. Vapor density measurements [15,16] and infrared absorption studies [17] have also pointed to the existence of the higher polymers. Renner et al. [18] have detected tetrameric methanol in the gas phase at around 325 K by thermal conductivity measurements. Van Thiel et al. [19] carried out a study of methanol suspended in solid nitrogen at 20 K. Their paper provides the first identification of discrete absorptions due to the various multimer species present in methanol. Their investigation covered the $\nu(OH)$ and ν (CH) spectral region 2800–3700 cm⁻¹, and by varying the concentration over matrix: absorber (M/A) ratio 2220 to 10, they were able to assign bands to monomer (cyclic) dimer (cyclic) trimer and

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tetramer, as well as to higher polymers. Barnes and Hallam [20] reported the infrared spectra between 40 and 4000 cm⁻¹ for CH₃OH and CH₃OD, and between 650 and 4000 cm⁻¹ for CD₃OD, ¹³CH₃OH and CH₃ ¹⁸OD suspended in argon matrices at 20 K. They recorded the spectra of CH₃OH in argon matrices over a range of concentrations, from M/A = 2000 to 20, and were able to assign observed frequencies to monomer, multimer, open chain dimer, open chair trimer, open chain tetramer and high polymers. Del Bene [21] determined the structure and binding energy of the methanol dimer using a minimal basis set. Curtiss [22] extended these calculations to the series $(CH_3OH)_n$ (n = 3, 4, 5, 6). The relative stabilities of these polymers were used to explain and underscore some of the experimental observations on methanol in the gas phase. It was also found that cyclic structures are more stable than the open structures for the trimer and higher polymers. He also reasoned that the results of his study could be related to the structure of liquids, since it is not unreasonable to assume that there may be a number of cyclic polymers present in the liquid. Curtiss also pointed out that the change in binding energy with the addition of the *n*th molecule for the series $(CH_3OH)_n$ is largest for the tetramer. He emphasized that the larger cyclic structures are also more stable than their chain analogues. A detailed study by Provencal et al. [23] showed that methanol clusters larger than dimer must exist in cyclic ring configuration. In this regard, Pribble et al. [24] showed that the methanol tetramer structure in benzene is a cyclic tetramer

Regarding the methanol's vibrational modes, there has been many assignments for this molecule including: CH₃OH:vapor infrared [25–31], liquid infrared [32–36], liquid Raman [37–50], vapor Raman [45]; CH₃OD: vapor infrared [27,28,31,32,51], liquid infrared [31], liquid Raman [40,41,43]; CD₃OH and CD₃OD:vapor infrared [27,28,31,32,51,52]; CD₃OD:liquid Raman [27,46], solid CH₃OH [30,31,52] among which most extensive work has been done by Falk and Whalley [52]. These researchers have made a complete assignment of the internal modes by recording the infrared spectra of CH₃OH, CH₃OD, CD₃OH, and CD₃OD in different phases, including gas, liquid, vitreous solid, α -crystal, and β crystal in the 300–4000 cm⁻¹ range, and Raman spectrum of liquid CD₃OH. Therefore, we preferentially used their assignment in our work.

2. Experimental

The chemicals benzene and methanol were purchased from Merk. Benzene and methanol were distilled for further purification and measuring their boiling points at laboratory pressure (678 mmHg) the binary azeotrope were prepared by adding appropriate quantities of the liquids by volume, using micropipettes. The mixture were fractionally distilled and a center fraction boiling at 55.3 °C was chosen from the same multiplate column. The mid-IR spectra of benzene, methanol, and azeotrope were recorded on a Nicolet 800 Fourier transform interferometer equipped with a high intensity Globar source, Ge/KBr beam splitter and DTGS detector. A resolution of 0.09 cm⁻¹ was utilized and 500 iterferograms were taken on both sample and empty reference cell. The Raman spectra were collected employing 180° back scattering geometry and a Bomen BM-154 Fourier Transform Raman Spectrometer. The Raman spectrometer equipped with a ZnSe beam splitter and a TE cooled InGaAs detector. Rayleigh filtering was afforded by two sets of two holographic technology filters. Laser power at the sample was 500 MW. The spectra were collected with a resolution of 2 cm^{-1} by coadding the results of 1000 scans. All ¹H NMR spectra for these studies were acquired on a Varian (VXR-500) 500 MHz pulsed NMR spectrometer with a 7.04T superconducting magnet. The spectra were obtained unlocked, which is possible due to the negligible field drift over the course of an experiment.



Fig. 1. FT-IR spectra of benzene (....), methanol(---), as well as their azeotrope (-) in the region 2400–3600 cm⁻¹.

3. Results and discussion

Benzene and methanol form a homogenous binary azeotrope with minimum boiling point in which the mole ratio of benzene to methanol is 2:3. Pure samples of benzene and methanol boil at 61 and 76 °C (at 678 mmHg), respectively, while their azeotrope boils at 5576 °C. The 2176 °C decrease in boiling point of benzene and 676 °C decrease in boiling point of methanol shows that attraction forces between benzene molecules has been obviously diminished in the azeotrope. Boiling point depression of benzene is significantly more than that of methanol. This difference indicates that benzene molecules must be noticeably much more separated from each other by loosing their original attraction forces, due to the azeotrope formation.

In hydrogen bonded molecules, such as methanol, the O–H stretching vibration is one of the more powerful and sensitive probes of the intermolecular hydrogen bond. The O–H stretch is sensitive to the strength, type, and number of hydrogen bonds in which it participates, because it vibrates directly against the hydrogen bond. When a hydrogen bond is present the O–H stretch fundamental shifts its frequency to the red, increases in breath, and typically increases in intensity [53,54].

Figs. 1 and 2 show that the O–H stretching mode of methanol has been red shifted. This frequency has been moved from 3354.1



Fig. 2. FT-IR spectra of benzene (...), methanol(---), and benzene–methanol azeotrope (-) in the region 500–1600 cm⁻¹.

Table 1

Vibrational frequencies of benzene, methanol, and benzene-methanol azeotrope, along with frequency shifts in azeotrope with respect to corresponding bands in pure substances^a.

Vibrational mode	Benzene(cm ⁻¹)		Methanol(cm ⁻¹)		Azeotrope (cm ⁻¹)		Δ (cm ⁻¹)	
	IR	Raman	IR	Raman	IR	Raman	IR	Raman
OH a. str.			3354.1		3350.2		-3.9	
C–H a. str.	3090.7				3091.7		1	
C–H a. str.	3071.1				3071.9		0.8	
C–H s. str.		3061.9				3063.1		1.2
C–H a. str.	3045				3045.8		0.8	
C–H s. str.		3035.7				3036.9		1.2
C–H a. str.	3034.8				3035.7		0.9	
CH₃ a. str.			2944.5		2943		-1.5	
CH ₃ s. str.				2940.8		2940.3		-0.5
CH ₃ s.str.				2833.5		2832.7		-0.8
CH₃ s.str.			2832.3		2831.2		-0.9	
C–H i.p. bend		1583.8				1586.7		2.9
CH ₃ s. def.		1451.6				1449		-2.6
C–H i.p. bend		1178.8				1177.1		-1.7
CH ₃ rock	1114.2				1115.5		1.2	
C–O str.		1035				1036		1
CCC bend	673				678		5	
OH o.p. bend			654		654.5		0.5	
OH i.p. bend				604		606.7		2.7

^a Only those frequencies which have observable and/or have measurable frequency shifts are listed.

to 3350.2 cm^{-1} upon azeotrope formation (Table 1). This red shift shows that a rather stronger hydrogen bonding is formed between methanol molecules in the azeotrope. Obviously, 3.9 cm^{-1} decrease in O–H stretching mode shows that methanol's cyclic polymers (CH₃OH)_n, with *n* = 4 have gained their most stable association form by formation of the tetramer [22,55]. As mentioned by Davies [35], the potential field governing all the vibrations of the group will be influenced simultaneously. Thus, in the case of a hydroxyl group, while interaction with another molecule will stretch the O–H bond and so cause decease in the valence frequency, it will tend to tie the hydrogen more firmly in its angular orientation. Accordingly, the deformation frequency can be expected to rise on association. Figs. 3 and 4 and Table 1 show that this has actually occurred for O–H bending mode, upon azeotrope formation.

It is also expected that symmetric and asymmetric stretching vibration of methyl group in methanol shift toward lower wavenumbers upon formation of stronger hydrogen bonding between hydroxyl groups in cyclic polymers. Hydrogen bonding between hydrogen of one alcohol and nonbonding electrons on neighbouring molecule, reduces the electron density in the vicinity of the foregoing oxygen, therefore, this oxygen pulls methyl group toward itself more than methanol's individual state, this inductive effect relatively weakens the C-H bond, the result is a red shift in the C–H stretching modes. As it can be seen in Figs. 1 and 2 and Table 1. this is exactly what we have observed. Formation of tetramers in azeotrope causes stronger hydrogen bonding between methanol molecules which moves CH₃ asymmetric stretching modes shift from 2944.5 and 2832.3 cm⁻¹, to 2943 and 2831.2 cm⁻¹, respectively. As we mentioned in the previous paragraph, when stretching vibration in a special group shows blue shift, the deformation vibrations show red shift, and vice versa. In azeotrope the deformation as well as the rocking modes of methyl groups exhibit significant peak shifts in the presence of benzene. Here, as we discussed above, since stretching modes show red shift, we expect blue shift for all deformation modes in CH₃ moiety. Figs. 3 and 4 show that this is actually the case. CH₃ asymmetric deformation, symmetric deformation and CH_3 rock show 0.3, 3.3, and 1.2 cm⁻¹ blue shift in their vibrational spectrum (Table 1). Regarding the methanol moiety, the O-H bond is lengthened substantially while the C-O bond is shortened. Such a structure change seems to be reflected in the red shift of the O-H stretching mode and the blue shift of the C-O stretching mode, due to the stronger H-bonding, the O-H bending mode is significantly blue shifted. Fig. 2 shows that upon formation of



Fig. 3. FT-Raman spectra of benzene (....),methanol(---), and their azeotrope (-) in the region 500–1700 cm⁻¹.



Fig. 4. FT-Raman spectra of benzene (....), methanol(---), and their azeotrope (-) in the region 2700–3200 cm⁻¹.

Table 2

Proton chemical shift data for benzene, methanol, and their azeotrope.

Substance	Proton in	δ (ppm)	δ (ppm) in azeotrope	$\Delta\delta$ (ppm)
Benzene	C-H	7.1495	7.2504	0.1009
Methanol	OH CH₃	4.9447 3.3554	4.9577 3.3614	0.013 0.006

azeotrope, the C–O stretching mode in methanol has been shifted from 1034 to 1036 cm⁻¹ (Table 1).

Concerning benzene's vibrational assignments, several studies have appeared on the frequencies of benzene [56-61]. The experimental frequencies of benzene reported in liquid state [56,57] and in the gas phase [58], and theoretical estimations for the harmonic frequencies [62,63] are also reported. Among these assignments, the work of Wilson [56] looks more satisfactory, therefore, his assignments are used in our work. Although benzene molecules don not have electric dipole, they have six lonepair-unlocalized electrons which produce strong Van der Waals attraction forces, causing high boiling point for this neutral substance, so we expect that on vaporization, or making solutions with appropriate media, these forces diminish and/or vanish, depending on the matrix. As the result of reduction of intermolecular attraction forces, C-H stretching modes become more independent and less affected by neighbouring molecules, consequently these modes need more energy to vibrate which means a blue shift in their infrared and Raman spectra. 21 °C depression in benzene's boiling point shows that these molecules are widely separated from each other in azeotrope which confirms the cause of blue shift for these C-H stretching modes, and this is exactly what we observed (Figs. 1 and 2). Table 1 shows that all C-H stretches and in plane modes are shifted toward the higher frequencies. Among all bending modes of benzene, only out of plane motions show red shift in IR spectrum (Figs. 3 and 4, and Table 1). This can be attributed to the orientation of benzene molecules in the azeotrope. We can imagine that oxygen's lone pair electrons in methanol are directed toward the hydrogen atoms in benzene, which eases hydrogen's out of plane bending mode, as a result of this newly formed attraction, this mode shifts to the lower frequency.

Table 2 shows that the CCC bending mode in benzene is shifted to the higher frequency, this frequency change can be explained as below: in liquid benzene, alignment of molecules causes a harmonic and in phase bending motion in which molecules need less energy to vibrate, while, on vaporization or dilution, where benzene molecules are separated and attraction forces between adjacent molecules are diminished, benzene molecules loose their harmony and need more energy to do ring bending vibration, therefore need more energy for doing the same vibration, which means a blue shift in the vibrational spectrum. Fig. 3 and Table 1 show that the CCC bending mode has been shifted from 673 to 678 cm⁻¹, which confirms above prediction.

In the case of NMR, shielding affects the $\delta({}^{1}\text{H})$ chemical shift frequencies. The observed chemical shifts for the CH₃ and OH groups in methanol and C–H in benzene are extremely sensitive to changes in their local orientations. The proton in OH moiety can be used to study changes in the hydrogen bond. The use of NMR chemical shifts in conjunction with molecular simulations allows one to establish an appropriate physical model describing the effect of different factors on the extent of hydrogen bonding for these liquids. In methanol's tetramer, with stronger hydrogen bonding, oxygen atom of each molecule attracts hydroxyl proton on the adjacent molecules stronger than before, consequently its high electron density pulls protons stronger, in comparison with other multimers in the liquid, toward itself, which removes bonding electrons partially and causes deshielding of such protons. Also



Fig. 5. ¹H NMR spectra of benzene, methanol, and their azeotrope.

when azeotrope forms, due to the attraction between benzene protons and lone pair electrons on hydroxyl moiety, the C-H band stretches out causing an electron density decrease in the vicinity of these protons. For benzene protons, base on boiling point depression and IR spectrum, which indicate that intermolecular attraction forces are reduced by azeotrope formation, we anticipate deshielding for these protons. High electron density of the media pulls the benzene protons toward itself and reduces the electron cloud around proton, which results deshielding of protons in benzene. Experimentally, we have observed 0.1009 ppm deshielding for benzene protons (Fig. 5 and Table 2) which indicates that benzene molecules are not only disaggregated, but are distributed among methanol tetramers in such a way that their hydrogens have been attracted by the oxygens of hydroxyl groups. Similarly, we can predict that in comparing methanol tetramer with liquid methanol, where weaker hydrogen bondings are present, bonding electrons in hydroxyl group are relatively more deshielded, therefore, we expect deshielding for these protons too. Fig. 5 shows that proton signal in the O-H moiety in azeotrope has been shifted toward higher chemical shift ($\Delta \delta = 0.013$ ppm) which verifies above prediction. In agreement with IR results, which shows red shift for C-H stretching modes of methyl group, we expect deshielding for these



Fig. 6. Orientation of methanol tetramers to form benzene-methanol azeotrope.



Fig. 7. Proposed unit-structure of the benzene-methanol azeotrope, methyl groups are not shown for better visualization.

protons. Fig. 5 and Table 2 show that methyl protons are shifted from 3.3554 ppm in liquid methanol to 3.3614 ppm in the azeotrope ($\Delta \delta$ = 0.006 ppm).

Based on vibrational (FT-IR and Raman), and ¹H NMR spectral changes, boiling point depression of benzene and methanol, and mole ratio of constituents in the azeotrope, the following structures have been proposed for the orientation of the methanol tetramer (Fig. 6) and unit-structure of the azeotrope (Fig. 7) with formula $[(CH_3OH)_4]_3[C_6H_6]_8$.

Assuming the proposed structure (Fig. 7) as unit-structure of the cluster, we can describe all observed changes:

- (i) The mole ratio of benzene to methanol in this structure is in accord with experimental results (2:3).
- (ii) The tetramer structure of methanol and indifferent distribution of them in the azeotrope are being considered.
- (iii) Formation of methanol tetramers with stronger hydrogen bonding can easily explain the red shift of OH moiety in vibrational spectra and deshielding of O–H proton signal in ¹H NMR spectrum.
- (iv) Benzene molecules are indifferently distributed in the azeotrope, so that they cannot show any additional band or signal in the azeotrope's spectra.
- (v) Location of methyl groups in the vicinity of the benzene ring cause $H-\pi$ binding, which can explain red shift and blue shift for stretching and deformation vibrations of methyl groups, respectively.
- (vi) Benzene molecules' orientation around the tetramers is so that they are completely isolated from each other, which can cause benzene's high boiling point depression in the azeotrope.
- (vii) Isolation of benzene molecules in the azeotrope, in comparison with pure liquid benzene, not only causes the reduction of intermolecular forces, but also shifts the C–H stretching signal to the higher frequency (blue shift).
- (viii) Closeness of oxygen's lone pair electrons (which are symmetrically and homogeneously distributed) with benzene molecules can easily explain the benzene's protons deshielding in NMR spectrum.
- (ix) Majority of molecules in the azeotrope are methanol ones $[(CH_3OH)_4]_3 [C_6H_6]_8$, so boiling point depression for this molecule must be less than benzene.
- (x) Distribution and orientation of molecules in the unitstructure of cluster (Fig. 7) is indiscriminately and completely reasonable so that, all functional groups have similar situation.

4. Conclusion

Based on decrease in boiling point of benzene and methanol, mole ratio of these molecules in the azeotrope, FT-IR, FT-Raman, and ¹H NMR spectral analysis, the unit-structure of benzene–methanol azeotrope have been deduced. The proposed structure can completely explain boiling point depression of constituent molecules and all FT-IR, FT-Raman, and ¹H NMR spectral changes due to the azeotrope formation.

References

- [1] M. Magini, G. Paschina, G. Piccaluga, J. Chem. Phys. 77 (1982) 2051.
- [2] M. Haughney, M. Ferraio, I.R. McDonald, Mol. Phys. 58 (1986) 849.
- B.M. Pettitt, P.J. Rossky, J. Chem. Phys. 78 (1983) 7296.
 J.F. Mammone, S.K. Sharma, M. Nicol, J. Phys. Chem. 84 (1980) 3130.
- [5] A.H. Narten, A. Habenschuss, J. Chem. Phys. 80 (1984) 1984.
- [6] D.G. Montague, I.P. Gibson, J.C. Dore, Mol. Phys. 44 (1981) 1355.
- [7] W.L. Jorgensen, M.I. Ibrahim, J. Am. Chem. Soc. 104 (1982) 373.
- [8] J. Jonas, J.A. Akai, J. Chem. Phys. 66 (1977) 4946.
- [9] E.M. Schulman, D.W. Dwyer, D.C. Doetschman, J. Phys. Chem. 94 (1990) 7308.
- [10] J.G. Oldenziel, N.J. Trappeniers, Physica A 83 (1976) 161.
- [11] S.L. Wallen, B.J. Palmer, B.C. Garrett, C.R. Yonker, J. Phys. Chem. 100 (1996) 3959.
- [12] W. Weltner, K.S. Pitzer, J. Am. Chem. Soc. 73 (1951) 2606.
- 13] G.S. Kell, G.E. McLaurin, J. Chem. Phys. 51 (1969) 4345.
- [14] E.E. Tucker, S.B. Farnham, S.D. Christian, J. Phys. Chem. 73 (1969) 3820.
- [15] C.B. Kretschmer, R. Wiebe, J. Am. Chem. Soc. 76 (1954) 2579.
- [16] V. Cheam, S.B. Farnham, S.D. Christian, J. Phys. Chem. 74 (1970) 4157.
- [17] R.G. Inskeep, J.M. Kelliher, P.E. McMahon, B.G. Somers, J. Chem. Phys. 28 (1958) 1033.
- [18] T.A. Renner, G.H. Kucera, M. Blander, J. Chem. Phys. 66 (1977) 177.
- [19] M. Van Thiel, E.D. Becker, G. Baglin, J. Chem. Phys. 49 (1968) 2106.
- [20] A.J. Barnes, H.E. Hallam, Trans. Faraday Soc. 66 (1970) 1920.
- [21] J. Del Bene, J. Chem. Phys. 55 (1971) 4633.
- [22] L.A. Curtiss, J. Chem. Phys. 67 (1977) 1144.
- [23] R.A. Provencal, J.B. Paul, K. Roth, C. Chapo, R.N. Casae, R.J. Saykally, G.S. Tschumper, H.F. Schaefer, J. Chem. Phys. 110 (1999) 4258.
- [24] R.N. Pribble, F.C. Hagemeister, T.S. Zevier, J. Chem. Phys. 106 (1997) 2145.
- [25] L.I. Kinsey, J.W. Ellis, J. Chem. Phys. 5 (1937) 399.
- [26] A. Borden, E.F. Barker, J. Chem. Phys. 6 (1938) 553.
- [27] H.N. Noether, J. Chem. Phys. 10 (1942) 693.
- [28] B.I. Stepanov, J. Phys. Chem. (U.S.S.R.) 19 (1945) 497.
- [29] E.K. Plyler, J. Res. Natl. Bur. Standards 48 (1952) 281.
- [30] A.V. Stuart, G.B.B.M. Sutherland, J. Chem. Phys. 24 (1956) 559.
- [31] P. Tarte, R. Deponthiere, Bull. Soc. Chim. Belg. 66 (1957) 525.
- [32] J.R. Quinan, S.E. Wiberely, J. Chem. Phys. 21 (1953) 1896;
 J.R. Quinan, S.E. Wiberely, Anal. Chem. 26 (1954) 1762.
- [33] A.M. Buswell, V. Deitz, W.H. Rodebush, J. Chem. Phys. 5 (1937) 501.
- [34] D.R. McMillan Jr., Phys. Rev. 57 (1940) 941.
- [35] M. Davies, J. Chem. Phys. 16 (1948) 267.
- [36] F.A. Smith, E.C. Creits, J. Res. Natl. Bur. Standards 46 (1951) 145.
- [37] S. Venkateswaran, Phil. Mag. 15 (1933) 263.
- [38] B. Trumpy, Kgl. Norske Videnskab. Selskabs Skrifter 1 (1934) 1.
- [39] E. Bartholome, H. Sachsse, Z. Phys. Chem. B30 (1935) 40.
- [40] R.G. Loyarte, J.S. Fernandez, Contrib. estud. cienc. fis. Y mat. (La Plata) 1 (1935) 3.
- [41] S. Mizushima, Y. Morino, G. Okamoto, Bull. Chem. Soc. Japan 11 (1936) 698.
- [42] R. Bates, L.C. Anderson, J.O. Halford, J. Chem. Phys. 4 (1936) 535.
- [43] J.O. Halford, L.C. Anderson, G.H. Kissin, J. Chem. Phys. 5 (1937) 927.
- [44] J. Wagner, Z. Phys. Chem. B40 (1938) 36.
- [45] J.R. Nielsen, N.E. Ward, J. Chem. Phys. 10 (1942) 81.
- [46] M. de Hemptinne, T. Doehaerd, Bull. Acad. R. Belg. Ser. 5 (30) (1944) 189.
- [47] A.L.S. Rao, J. Indian Chem. Soc. 22 (1945) 260.
- [48] P.K. Narayanaswamy, Proc. Indian Acad. Sci. A 26 (1947) 121.
- [49] W.G. Braun, D.F. Spooner, M.R. Fenske, Anal. Chem. 22 (1950) 1074.
- [50] H. Nakamura, I. Obata, Busseiron Kenkyu 85 (1955) 36;
- H. Nakamura, I. Obata, Chem. Abstr. 50 (1956) 5406.
- [51] E.F. Barker, G. Bosschieter, J. Chem. Phys. 6 (1938) 563.
- [52] M. Falk, E. Whalley, J. Chem. Phys. 34 (1961) 1554.
- [53] G.C. Pimental, A.L. McClellan, The Hydrogen Bond, Freeman, San Francisco, 1960.
- [54] J.C. Pore, J. Texcira, Hydrogen-Boned Liquids, Khuwer, Dordrecht, 1991.
- [55] M. Van Thiel, E.D. Becker, G. Baglin, J. Chem. Phys. 27 (1957) 95.
- [56] E.B. Wilson, Phys. Rev. 45 (1934) 706.
- [57] G. Varsanyi, Assignment for Vibrational spectra of Seven Hundred Benzene Derivatives, Adam Hilger, London, 1970.
- [58] L. Goodman, A.G. Ozkabak, S.N. Thakur, J. Phys. Chem. 95 (1991) 9044.
- [59] G. Ranhut, P. Pulay, J. Phys. Chem. 99 (1995) 3093.
- [60] S.N. Thakur, L. Goodman, A.G. Ozkabak, J. Chem. Phys. 84 (1986) 6642.
- [61] G. Baranovic, B. Schrader, J. Mol. Struct. (Theochem.) 306 (1994) 165.
- [62] N.C. Handy, P.E. Maslen, R.D. Amos, J.S. Andrews, C.W. Murray, G. Laming, J. Chem. Phys. Lett. 197 (1992) 506.
- [63] M.P. Alcolea, Int. J. Quant. Chem. 77 (2000) 661.