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HETEROMOLECULAR STRUCTURE FORMATION IN BINARY SOLUTIONS OF DIMETHYLFORMAMIDE-WATER AND TETRAHYDRAFURAN-WATER: FTIR AND REFRACTOMETRY.

Abstract. Along with other works where the authors use a more complex and time-consuming approach to analyze the formation of heteromolecular structures in aqueous solutions of dimethylformamide and tetrahydrofuran, we propose a new technique based on the combined use of refractometry and IR spectroscopy. The formation of intermolecular complexes is analyzed by measuring the excess refractive index and the ratio of OH absorption bands of bound molecules to those of free ones in the concentration range of 0÷1 mole fraction of components. It was shown that the formation of heteromolecular structures occurs in a narrow concentration range of 0.3÷0.4 mole fractions of dimethylformamide and tetrahydrofuran, which corresponds to the maximum number of realized hydrogen bonds in the dimethylformamide-water and tetrahydrofuran-water systems.

Key words: Infrared spectroscopy, excess refractive index, heteromolecular structures.

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ФОРМИРОВАНИЕ ГЕТЕРОМОЛЕКУЛЯРНОЙ СТРУКТУРЫ В БИНАРНЫХ РАСТВОРАХ ДИМЕТИЛФОРМАМИД-ВОДА И ТЕТРАГИДРАФУРАН-ВОДА: ИК-ФУРЬЕ-СПЕКТРОСКОПИЯ.

Аннотация. Наряду с другими работами, в которых авторы используют более сложный и трудоемкий подход к анализу образования гетеромолекулярных структур в водных растворах диметилформамида и тетрагидрофурана, нами предлагается новая методика, основанная на совместном использовании рефрактометрии и ИК-спектроскопии. Анализ образования межмолекулярных комплексов проводится путем измерения избыточного показателя преломления и отношения полос поглощения ОН связанных молекул к полосам поглощения свободных в диапазоне концентраций 0÷1 мольных долей компонентов. Показано, что образование гетеромолекулярных структур происходит в узком диапазоне концентраций 0.3÷0.4 мольных долей диметилформамида и тетрагидрофурана, что

соответствует максимальному числу реализуемых водородных связей в системах диметилформамид-вода и тетрагидрофуран-вода.
Ключевые слова: Инфракрасная спектроскопия, избыточный показатель преломления, гетеромолекулярные структуры.

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DIMETILFORMAMID-SUV VA TETRAGIDROFURAN-SUV BINAR ERITMALARIDA GETEROMOLEKULYAR TUZILMALAR SHAKLLANISHINI INFRAQIZIL SPEKTROSKOPIYA VA REFRAKTOMETRIYA METODLARI ORQALI

Annotatsiya. Mualliflar dimetilformamid va tetragidrofuranning suvli eritmalarida geteromolekulyar tuzilmalarning shakllanishini tahlil qilish uchun murakkabroq va ko‘p vaqt talab qiladigan yondashuvdan foydalanadigan boshqa ishlar bilan bir qatorda, refraktometriya va IQ spektroskopiyadan birgalikda foydalanishga asoslangan yangi texnikani taklif qilindi. Molekulalararo komplekslarning hosil bo‘lishi ortiqcha nur sindirish ko‘rsatkichini va komponentlarning 0÷1 mol ulushi konsentratsiya oralig‘ida molekulalarning OH yutilish zonalarining erkinliklari nisbatini o‘lchash metodi orqali tahlil qilinadi. Geteromolekulyar tuzilmalarning hosil bo‘lishi dimetilformamid va tetragidrofuranning 0.3÷0.4 mol ulushli konsentratsiyasi oralig‘ida sodir bo‘lishi

ko‘rsatildi, bu dimetilformamid-suv va tetragidrofuran-suv tizimlarida hosil bo‘lgan vodorod aloqalarining maksimal soniga to‘g‘ri keladi.

Kalit so‘zlar: Infraqizil spektroskopiya, ortiqcha nur sindirish ko‘rsatkichi, geteromolekulyar tuzilmalar.

Introduction

There are various experimental methods for investigating the properties of water and aqueous-organic solutions: dielectric and infrared spectroscopy, Raman spectroscopy, and terahertz spectroscopy, X-ray diffraction, neutron diffraction, proton magnetic resonance spectroscopy and others. All these methods are highly sensitive to various structural and relaxation changes in molecules of liquids, allowing to establish specific mechanisms of their mutual dissolution in a wide range of component concentrations and solution temperatures and to register the formation of mono- and heteromolecular associates in solutions, as well as clathrate formations in aqueous mixtures almost any organic solvents.

Understanding the processes of hydrogen bond formation plays a significant role in determining the structure and physicochemical properties of many structures and materials, and is intensively studied in physics, chemistry, biology, and interdisciplinary research. Systems with hydrogen bonds find use in various applied studies, for example, in crystal design [1], in the creation of systems with self-assembly [2,3] and molecular recognition [4,5], in hydrothermal synthesis [6,7] and others.

The refractometric parameters and their excess values make it possible to understand structural changes in binary and ternary solutions and provide valuable information about intermolecular interactions. Thus, a review of the literature shows that there are no reports studying the combination of infrared spectroscopy and refractometry for aqueous solutions of dimethylformamide (DMF) and tetrahydrofuran (THF).

Experimental section

Materials

Standard grade tetragidrofuran (C_4H_8O) (minimum assay 99.9 wt.%) and N,N-dimethylformamide (C_3H_7NO) (purity ~99.9 wt.%) obtained from Reagent Plus, as well as distilled water with pH=7.02 were used in the experiments. Each aqueous-organic solution of a given composition was prepared separately and was

not used in the preparation of solutions with different concentration of compositions.

Measurement

Refractive indices were measured using a high-sensitivity PAL-RI digital refractometer (ATAGO, Japan). The instrument measures refractive indices in the range of 1.3306-1.5284, the measurement error n is <0.0001.

Fourier transform infrared spectra were recorded on a Perkin Elmer Spectrum Two spectrophotometer with a signal-to-noise ratio of 9300:1 and a resolution of 0.5 cm^{-1} on a LiTaO3 detector. The spectra of pure water, DMF, THF, and their mixtures were recorded in the wavelength range of 4000-400 cm^{-1}.

Results and discussion

Refractometric properties

The excess refractive indices in terms of refractive index of pure liquids and their binary solutions of molar composition x were calculated using the equation:

$$n^E = n_{mix} - (x_1 n_1 + x_2 n_2)$$

Where x_1, x_2, n_1 and n_2 are the mole fractions and refractive indices of the first and second solvents in their solutions, respectively, and n_{mix} is the refractive index of the solution.

The stability of the temperature in the measurement compartment was controlled by a built-in thermostat on a Peltier element. The duration of measuring the refractive index of each sample of the solution was no more than 5 seconds. 0.3 ml solution of each sample by three times was measured to make sure measurement accuracy, and to avoid equipment error.

In the THF-water and DMF-water systems, the refractive index values change monotonically with increasing molarity of aprotic liquids. The refractive indices of the THF-water and DMF-water systems show a positive value along the x-axis (Figure 1).

The maximum of excess refractive indices corresponds at 0.3÷0.4 mole fraction of DMF and THF in the water. This is a good agreement with other literature data [8,9]. This result indicates that solvent-solvent interaction of DMF-

water is stronger in the same molar ratio of DMF and THF with water. Unlike the THF, the existence of nitrogen in the DMF makes both donor and acceptor bonds in the solution, and strengthens bonds between molecules DMF and water.

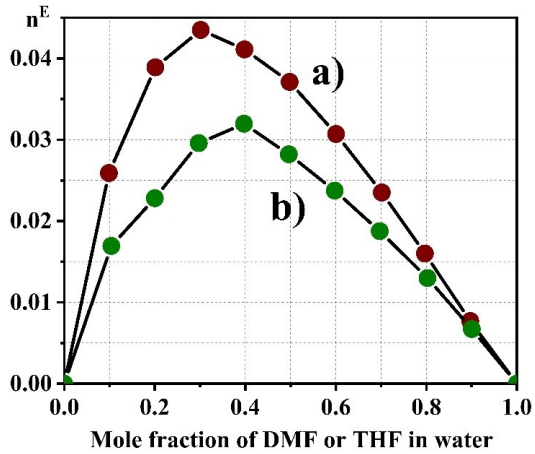

Figure 1. Excess refractive index for binary solutions of DMF-water (a) and THF-water (b).

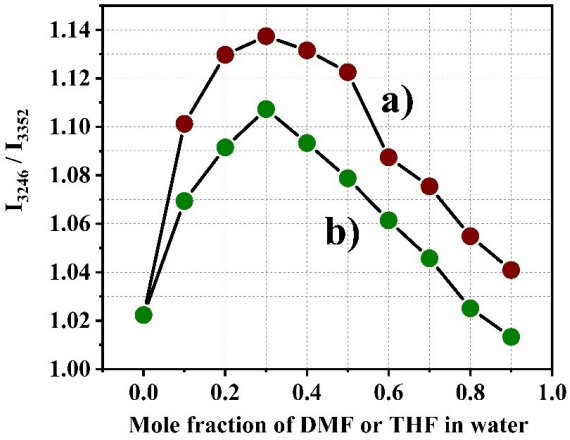

Figure 2. – Ratio of absorbance values taken at wavenumbers 3246 and 3360 cm^{-1} as a function of DMF (a) and THF (b) concentrations in solution.

Infrared spectra

Vibrational spectroscopy affords is a big and rare information about the bonding inter and inner molecular interactions in liquids. Investigate of vibrational frequency, changes in intensity and bandwidth give great understandings on which type intermolecular interactions are occurred in the liquid state. The infrared spectra of binary solutions of DMF-water and THF-water with concentration range 0-1 mole fraction was recorded. Fig. 3 shows IR spectra of DMF-water (Fig. 2a) and THF-water (Fig. 3b) at 3700-3000 cm^{-1} region.

The peak of maximum intensity in the spectra of DMF-water and THF-water is located at around 3400 cm^{-1}. Extremely wide spectra of OH stretching of both DMF-water and THF-water solutions, undergo changes in its integral intensity, also in the contour shape and the ratio of intensities taken at low frequency to high-frequency field. The absorption band 3352 cm^{-1} of DMF-water shifts to 3500 cm^{-1}, absorption band of THF-water at 3352 cm^{-1} shifts to 3450 cm^{-1} as shown in Fig.3b,

these shifts in the OH stretching region indicate strong hydrogen bonding interactions between DMF and THF, respectively, with water molecules (Fig. 3a).

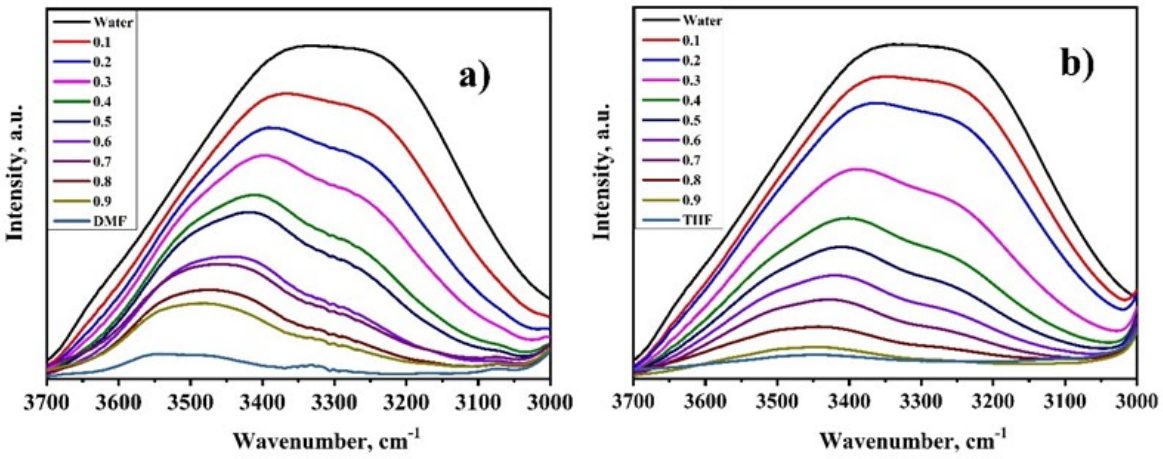

Fig. 3 – Absorption bands 3000-3700cm^{-1} of OH-groups in infrared spectra of DMF-water (a), and THF-water (b) solutions.

At X_{DMF} < 0.4, hydrogen bonds between DMF and water molecules occur rapidly as a result of the disruption of the tetrahedral structure of water or the breaking of hydrogen bonds between water molecules. Results exothermic enthalpies of DMF-water solution showed at x ≈ 0.33 mole fraction of DMF the repulsive interaction between the hydrophobic groups (CH_3) and water caused to clusters larger and long lived. This repulsive interaction leads to energy being released and that the hydrogen bonds between DMF and water are stronger than hydrogen bonds between water molecules.

According to the measured IR spectra it was shown that the mixture of water + THF forms complexes of 1:2 composition in the concentration range 0.1<x<0.4. It was shown that the hydration of THF occurs with the participation of weak hydrogen bonds $H_2O\cdots$H-C. It was shown that in a narrow concentration range of 0.25-0.4 mole fraction of THF the excess molar volume has a maximum characterizing the formation of a dense structural packing of mixtures accompanied by strong interactions between molecules of both components [8, 10]. Excess molar volumes for the tetrahydrofuran + water system were calculated

from experimentally measured densities and correlated using the Redlich-Kister equation [11].

DMF-water owns wide maximum peak position which includes 0.2-0.5 mole concentration of DMF in water, signified 0.3 mole DMF has strongest H-bonding, other concentration like 0.2 and 0.4 are closely make H-bonds in the solution. THF-water showed very sharp maximum of the peak at 0.3 mole fraction of THF in water, which is informs 0.3 THF owns distinguishable strong H-bonds than that other concentration. This result shows that hydrogen bond strengthening and significant structural rearrangement occur in the concentration range of $0.3<x<0.4$ mole fraction of DMF and THF. Both graphs show that the ratio passes through a maximum in the dissolved component concentration region of 0.3÷0.4 mole fraction. Comparative analysis of hydrogen bonding shows that water molecules are more strongly bonded to DMF than to THF. This IR analysis is in good agreement with the properties of H-bonds predicted by the refractive index excess. According to the purpose of the work, these two methods of analysis, complementing each other, are advantageous in obtaining quick and accurate information on H-bonds in the structure.

In the previous work [12], the ratio of absorption intensities at 3240 and 3360 cm^{-1} oscillation frequencies of OH-groups bound by strong and weak H-bonds for IR spectra of water-ethanol solutions are shown. This ratio of absorption intensities by concentration of components allows to get information of stronger and quantity of H-bonds in solutions. In this work, we calculated the ratio of absorption intensities at 3246 cm^{-1} and 3352 cm^{-1} which corresponds strong and weak hydrogen bonding, respectively (Fig. 2).

In the case of THF-water, we observed clear boundary of changes at 0.3 mole of THF. Unlike the medium concentration effect of DMF on water molecules, THF enters into water molecules network which formed due to hydrogen bonds, and linearly effects into the structure of water by increasing its concentration. It can be seen, that critic point of the concentration of THF is 0.3, which maximum H bonds occur between molecules THF and water. By increasing

concentration of THF, hydrogen bonds weaken and decrease due to destroying water-water H-bonds, increases THF-THF structures in the solutions.

Conclusion

By analyzing the refractometry data in detail, it was found that structural changes occur for DMF-water at ~0.3 mole fraction of DMF and THF-water at ~0.4 mole fraction of DMF. The studied two-component mixtures of THF-water and DMF-water belong to the category of solutions, in which not only intramolecular but also intermolecular complexes with H-bonding are realized, leading to compaction of solutions. The latter is confirmed by positive values of the excess refractive indices of all three binary mixtures in the entire range of component concentrations ($0<X<1$). The established patterns of structural self-organization of binary solutions can be useful both in planning chromatographic experiments using two-component aqueous organic solvents as a mobile phase and in analyzing the results obtained.

Thus, a novel approach based on the combined use of refractometry and IR spectroscopy is proposed to study structural changes in DMF-water and THF-water solutions in the concentration range from 0.0 to 1.0 mole fraction of components at room temperature and atmospheric pressure. It is shown that refractometry and IR spectroscopy are not only simple and accessible in the study of aqueous solutions of aprotic solvents, but also extremely sensitive for detecting the formation of heteromolecular structures due to hydrogen bonds.

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Reference

1. A. M. Kokhkharov, E. A. Zakhidov, et al, Int. J. Nanosci. 12(4), 1350027 (2013).
2. R. B. Patel, V. Stepanov, H. Qiu, Appl. Spectrosc. 70(8), 1339-1345 (2016).

3. I. V. Plastinin, S. A. Burikov, Sh. P. Gofurov, O.B. Ismailova, et all, J. Mol. Liq. 298, 112053 (2020).
4. A. L. Cholli, M. L. Lau, Appl. Spectrosc. 43(7): 1168-1172 (1989).
5. O. B. Ismailova, T. Kh. Akhmedov, Kh. T. Igamberdiev, S. I. Mamatkulov, A. A. Saidov, S. O. Tursunov, P.K. Khabibullaev, 78(5), 1040-1045 (2005).
6. C. K. Larive, D. Jayawickrama, & L. Orfi, Appl. Spectrosc. 51(10), 1531-1536 (1997).
7. M. Flores-Castañeda, S. Camacho-Lopez, Opt. Laser Technol. 158, 108891 (2023).
8. M. Komudzińska, M. Tyczyńska, M. Jóźwiak, A. Burakowski, & J. Gliński. J. Mol. Liq. 300, 112321 (2020).
9. D Razzokov, O. B. Ismailova, Sh. I. Mamatkulov, O. V. Trunilina, A. M. Kokhkharov, Russ. J. Phys. Chem. A. 88, 1500-1506 (2014).
10. M. Katayama, & K. Ozutsumi, J Solution Chem. 37(6), 841-856 (2008).
11. G. Jones and S. K. Talley, J. Am. Chem. Soc. 55(2), 624-642 (1933).
12. S. Burikov, T. Dolenko, S. Patsaeva, Y. Starokurov, & V. Yuzhakov, Mol. Phys. 108(18), 2427-2436 (2010).