

## IR spectra of monoethanol amine and its binary mixtures in carbon tetrachloride

*N.V.Arhipenko, S.N.Kiyko, E.F.Ivanova*

V.Karazin Kharkiv National University,  
4 Svobody Sq., 61077 Kharkiv, Ukraine

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IR spectra of monoethanol amine and the monoethanol amine/acetonitrile and monoethanol amine/dimethylacetamide mixtures in  $\text{CCl}_4$  have been measured. The superposition of heteromolar interactions of monoethanol amine with acetonitrile and dimethyl acetamide onto the homomolecular interaction of monoethanol amine has been found to result in a lowered solvating ability of monoethanol amine in the binary mixtures.

Получены ИК спектры моноэтаноламина и смесей моноэтаноламина с ацетонитрилом и диметилацетамидом в  $\text{CCl}_4$ . Установлено, что наложение гетеромолекулярных взаимодействий моноэтаноламина с ацетонитрилом и диметилацетамидом на гомомолекулярное взаимодействие моноэтаноламина приводит к уменьшению сольватирующей способности моноэтаноламина в бинарных смесях.

Monoethanol amine (MEA) is used widely in various fields of chemistry and chemical engineering, such as production of drugs, detergents, emulsifiers, water softeners, etc. Moreover, MEA is among the typical amino alcohols which are included in biologically important substances, e.g., amino sugars, etc.

To elucidate the specific features of MEA association in solutions, IR spectra of isomolar series of MEA/acetonitrile (AN) and MEA/dimethyl acetamide (DMAA) mixtures in  $\text{CCl}_4$  were studied. The binary mixture concentrations in the solution was about  $0.05 \text{ mole/dm}^3$ . The pure MEA solutions in  $\text{CCl}_4$  at various MEA concentrations were studied, too. The substances used were purified as described in [1]. Freshly purified solvents were used to prepare the solutions. The pure MEA solutions and the MEA/DMAA and MEA/AN binary mixtures in  $\text{CCl}_4$  were prepared by weighing. The IR spectra were recorded using a Specord 75-IR spectrophotometer in the frequency range of  $3800\text{--}3000 \text{ cm}^{-1}$  at  $298 \text{ K}$ . A standard  $\text{CaF}_2$  cell of  $1 \text{ cm}$  optical length was used.

The IR spectra obtained for the MEA- $\text{CCl}_4$ , MEA/DMAA- $\text{CCl}_4$ , and MEA/AN- $\text{CCl}_4$  systems are presented in Figs. 1–3. Significant distinctions in those spectra draw attention. As to the MEA- $\text{CCl}_4$  system, four distinct bands peaked at  $3644$ ,  $3522$ ,  $3415$ , and  $3345 \text{ cm}^{-1}$  are seen. According to the available literature data [2, 3], the high-frequency  $3644 \text{ cm}^{-1}$  band is related to the  $\text{--OH}$  groups free of any hydrogen bond; thus, the MEA molecules can be assumed to be mainly in the *trans* form [4]. A weak shoulder at  $3621 \text{ cm}^{-1}$  is ascribed to the  $\text{--OH}$  group forming a bond with the amino hydrogen via one lone electron pair of oxygen, that is, the MEA molecules being in the *cis* form. The  $3522 \text{ cm}^{-1}$  band is characteristic of the bound  $\text{--OH}$  groups included in the MEA self-associates with inter- and intramolecular hydrogen bonds. Besides, the splitting of the bound  $\text{--OH}$  group band into two components is typical of IR spectra of MEA solutions in  $\text{CCl}_4$  as the solvent fraction increases. This evidences the presence of at least two MEA self-associate types, namely, the chain-like ones ( $3480 \text{ cm}^{-1}$ ) and five-member cycles ( $3522 \text{ cm}^{-1}$ ). Two

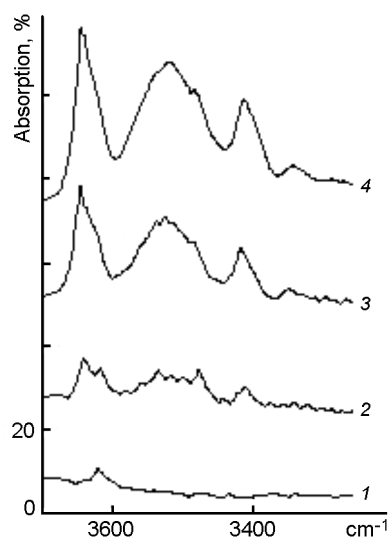


Fig. 1. IR spectra of MEA solutions in  $\text{CCl}_4$  at concentrations (mole/dm<sup>3</sup>): 0 (1), 0.0031 (2), 0.0061 (3), and 0.0124 (4).

bands at 3415 and 3345  $\text{cm}^{-1}$  answer to the asymmetric and symmetric vibrations of free  $-\text{NH}_2$  groups.

In Figs. 2 and 3, presented are IR spectra of MEA/DMAA- $\text{CCl}_4$  and MEA/AN- $\text{CCl}_4$  ternary mixtures. The small admixtures of AN and DMAA to MEA result in substantial changes of the spectra in the regions answering to the free and bound  $-\text{OH}$  groups of MEA as well as to the asymmetric and symmetric stretching vibrations of free  $-\text{NH}_2$  groups. The intensity of the band corresponding to the free vibrations of  $-\text{OH}$  groups in MEA (3644  $\text{cm}^{-1}$ ) decreases significantly and an additional broad band appears in the 3600–3200  $\text{cm}^{-1}$  region. The band of bound  $-\text{OH}$  groups in MEA (3522  $\text{cm}^{-1}$ ) decreases also in the intensity but at a lesser extent as compared to the 3644  $\text{cm}^{-1}$  one. These changes in the IR spectra of the MEA binary mixtures with non-electrolytes of various nature in  $\text{CCl}_4$  can be explained by the formation of MEA hetero-associates with AN and DMAA, the MEA molecules being in the *trans* form. This results in deterioration of the intrinsic network of H-bonds in MEA and an increased number of  $-\text{OH}$  and  $-\text{NH}_2$  group energy states causing the band overlapping both in pure MEA and in its hetero-molecular associates. Of considerable importance is the fact that the stretching vibration bands of free  $-\text{OH}$  groups are observable in the mixtures of various compositions. As the AN and DMAA content in the binary mixture increases, the intramolecular hydrogen

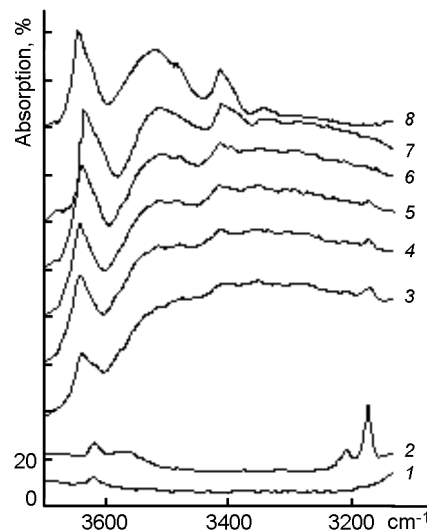


Fig. 2. IR spectra of MEA/AN binary mixtures solutions in  $\text{CCl}_4$  (0.05 mole/dm<sup>3</sup> of mixture): pure  $\text{CCl}_4$  (1), AN- $\text{CCl}_4$  (2), binary mixtures containing AN mole fraction 0.81 (3), 0.62 (4), 0.41 (5), 0.21 (6), 0.10 (7); MEA- $\text{CCl}_4$  (8).

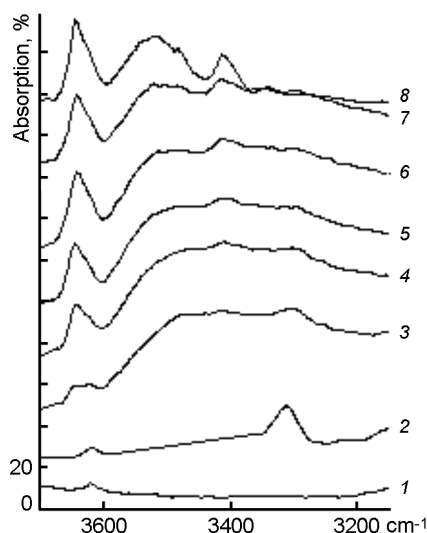


Fig. 3. IR spectra of MEA/DMAA binary mixtures solutions in  $\text{CCl}_4$  (0.05 mole/dm<sup>3</sup> of mixture): pure  $\text{CCl}_4$  (1), DMAA- $\text{CCl}_4$  (2), binary mixtures containing DMAA mole fraction 0.80 (3), 0.60 (4), 0.41 (5), 0.21 (6), 0.10 (7); MEA- $\text{CCl}_4$  (8).

bond in cyclic associates of *cis*-MEA breaks down and MEA/AN and MEA/DMAA associates are formed.

Thus, instead of four bands typical of MEA solutions in  $\text{CCl}_4$ , the MEA/AN and MEA/DMAA mixtures in  $\text{CCl}_4$  reveal the free stretching vibration band of  $-\text{OH}$  groups (3644  $\text{cm}^{-1}$ ) and a broad band

(3600–3200  $\text{cm}^{-1}$ ) being a sign of the H-bond formation between MEA and AN or DMAA. The MEA molecules in the hetero-associates are in the *trans* form. The intrinsic network of H-bonds in MEA becomes broken, that is apparent as the decreased intensity of the 3522  $\text{cm}^{-1}$  band.

It is to note also that the stretching vibrations of the free  $-\text{NH}_2$  groups both in pure MEA and in MEA/AN and MEA/DMAA systems in  $\text{CCl}_4$  met satisfactorily the empiric equation proposed by Bellami [5]

$$\nu_{sym} = 345 + 0.876 \cdot \nu_{asym} \quad (1)$$

that points also on a substantial fraction of free  $-\text{NH}_2$  groups in pure MEA and in the binary mixtures mentioned above.

Thus, the AN and DMAA admixtures in MEA must result in decreasing solvating ability of the mixed solvent as compared to that of pure MEA.

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## ІЧ спектри моноетаноламіну та його бінарних сумішей у розчині чотирихлористого вуглецю

*Н.В.Архипенко, С.М.Кійко, К.Ф.Іванова*

Отримано ІЧ спектри моноетаноламіну та сумішей моноетаноламіну з ацетонітрилом та диметилацетамідом у  $\text{CCl}_4$ . Встановлено, що накладення гетеромолекулярних взаємодій моноетаноламіну з ацетонітрилом та диметилацетамідом на гомомолекулярну взаємодію чистого моноетаноламіну, приводить до зменшення сольвативної здатності моноетаноламіну у бінарних сумішах.