O.O. ILCHENKO, V.V. NIKONOVA, A.M. KUTSYK, V.V. OBUKHOVSKY
Taras Shevchenko National University of Kyiv
(64, Volodymyrs'ka Str., Kyiv 01033; e-mail: radastasi@gmail.com)

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QUANTITATIVE ANALYSIS OF COMPLEX FORMATION IN ACETONE–CHLOROFORM AND ETHYL ACETATE–CYCLOHEXANE SOLUTIONS

The actual binary (double) solutions of "acetone–chloroform" and "ethyl acetate–cyclohexane" are simulated as ideal multi-component (triple, quadruple) mixtures, which consist of associates $[A_p]$, $[B_q]$, *and complexes* $[A_nB_m]$. *The MCR-ALS method is used for the analysis of near-IR absorption spectra. Complexes of a single type* $[A_1B_1]$ *are determined in an acetone–chloroform solution, and complexes of two types,* $[X_1Y_1]$ *and* $[X_5Y_1]$, *are determined in an ethyl acetate–cyclohexane solution. An auxiliary method for determining the number of complexes by analyzing the residual intensity in the IR spectra is proposed. Information about the number of complexes in solutions obtained by analyzing the residual intensity correlates with the MCR-ALS data. It is used for the interpretation of the formation of complexes in binary solutions.*

Keywords: acetone–chloroform, ethyl acetate–cyclohexane, complex, IR spectroscopy of solutions.

1. Introduction

A rigorous description of the structure of solutions requires the use of a statistical approach [1–3]. However, the simplified models are very useful. Thus, it is possible to assume that the mixture of two liquids A and B forms a multicomponent solution [4–6]. This solution can be considered as a mixture of the associates of pure components (further called – "associates") and mixed associates (further called – "complexes"). The structure of such complexes in an acetone–chloroform solution was determined a number of works [7–10]. It is well established that the interaction between the molecules of acetone and chloroform forms complexes with type 1:1. Some authors consider that, together with complexes type 1:1, complexes with type 2:1 also exist in a small amount [11, 12].

The determination of complexes in molecular spectra is associated with the degree of their occurrence in spectral bands. In this work, we will show that it is not possible to determine more than one complex type in an acetone–chloroform solution, the stoichiometric ratio of which can be assumed to be 1:1.

In some cases, the type of complexes can be predicted by the curve shape of the concentration dependence of the enthalpy $\Delta H(N_j)$, where N_j is the concentration of component A in component B, $N_j \in [1, 100]$. For example, if the last function has an extremum at 50 mol.%, this equation can be explained by the equality of molecules A and B in complex. The profile of the concentration dependence of the enthalpy in an acetone–chloroform solution is approximately symmetric with respect to an acetone concentration of 50 mol.% (minimum at 42 ± 3 mol.%) [13]. As a result, the consideration of the three-component model (with formation of only one type of complex) is an acceptable approximation.

The vibrational spectra analysis of liquid binary solutions with different concentrations of the components provides information about the concentration of structural formations in a solution [4, 14]. The se-

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lection of a spectral range for analysis is important in the chemometric processing of spectral data. The effects of intermolecular interactions appear with different degrees in different spectral bands. The studies of the concentration dependence of integrated intensities of the different vibrations for the acetone–chloroform solution were carried out by Raman spectroscopy in [15]. It was found that C–C and C–H vibrations of acetone (not involved in hydrogen bonding) are not shifted and broadened practically over the entire range of concentrations (0 to 100 mol.%) in the mixing process. But C=C vibrations of acetone and C-H vibrations of chloroform, directly involved in the hydrogen bonding in the complex, are undergoing significant changes. Moreover, the maximum increase in the integrated intensity of C=O vibrations of acetone accounted for a concentration of 45–50 mol.%.

A particular attention should be paid to the areas with the highest manifestation of the effects of intermolecular interactions in the selection of a spectral range. It is important to study the spectral bands with the least possible overlap of contours (it is one of the conditions for the successful application of the multivariate curve resolution method). The acetone–chloroform solution is of interest, because acetone is capable to forming a hydrogen bond with chloroform, while hydrogen bonds between molecules of acetone only or chloroform only are not formed. Note that the energy of the van-der-Waals interaction in associates (<1 kcal/mol) is less than the energy of the hydrogen bond (>3 kcal/mol [9])between the components in a complex $[A_nB_m]$. In this case, the distortion of the spectral lines associated with the emergence of associates A_p (consisting only of molecules of acetone) and B_q (consisting only of molecules of chloroform) will appear much weaker than the distortions connected with the appearance of complexes with type $[A_nB_m]$. Intermolecular interactions appear to a less extent in an ethyl acetate–cyclohexane solution due to the lack of hydrogen bonds between the molecules in the associates, as well as in the complexes, which makes it difficult to separate them from the IR absorption spectra.

The paper describes methods to determine the concentration of the structural formations (complexes) in acetone–chloroform and ethyl acetate–cyclohexane solutions. First, the amount and the concentration of complexes in a solution are determined, by using the chemometric method MCR-ALS [16] with respect to the absorption spectra in the near-infrared range. Next, an auxiliary method of determining the number of complexes by analyzing the residual intensity in the IR spectra is considered. A comparison of concentration values of the complexes obtained by MCR-ALS and by analyzing the residual intensity in the spectra is performed for acetone–chloroform and ethyl acetate–cyclohexane solutions. The correspondence of the results is found.

2. Experiment

Acetone, chloroform, ethyl acetate, and cyclohexane with a purity of 99.9% were used in this research. The concentration of components was changed from 0% to 100% (in volume %) with a step of 10%. The measurement of the spectra was carried out in 24 h after the time of the preparation of solutions to eliminate the influence of relaxation processes.

FT-NIR transmission spectra were measured with a Perkin Elmer Spectrum BXII spectrometer with a spectral resolution of 2 cm^{-1}. Spectra recording were repeated 10 times for every sample. Thereafter, the average spectra were calculated for every concentration and used in the further analysis. The spectra were not smoothed out by a software, and the baseline correction was not carried out (because these transformations can distort the manifestation of the effects of intermolecular interactions in the spectral bands). The optical path length of the quartz cell was 1 mm. Heating of the sample almost did not occur during the measurements due to a small value of the absorption coefficient at excitation frequencies. The temperature of liquid samples was 25 ± 0.2 °C.

3. Model Approach

3.1. The model of "binary" liquid solution

The binary solution is a mixture of two liquids A and B. However, there may be new components (a typical example – alcohol hydrates in aqueous alcohol solution). Subsequently, the "binary" solution will be considered as a mixture of the pure components A_q and B_q (associates) and complexes $[A_nB_m]$.

The term "complex" is used in different senses in the literature, so we focus on its definition. It is known that the lifetime of hydrogen and van-der-Waals bonds in molecular liquids is extremely small (less than $\approx 10^{-12}$ s) [18]. This raises the question of the appropriateness of the third component of the solution ("complexes") due to the instability of the compounds. However, the average lifetime of the complex τ_0 is only one characteristic. The second feature of the dynamics of the dissolution with the mean free time τ_f is the existence of molecules A and B. Suppose that $\tau_f = \tau_0$ and note that the macroscopic (measured) data correspond to averaging the relevant properties of an ensemble of particles over time $t \gg \tau_0, \tau_f$. In this case, 50% of the particles will always be in a bound state (complexes), and the remaining 50% of particles will be in the free (unbound) form in any physically infinitesimal volume. Within this approach, a small lifetime of intermolecular bonds does not matter, because the "complex" is considered as the average characteristics of the individual components of the system.

3.2. Analysis of residual intensity in the spectra

The spectra were measured at each fixed concentration of one component. A set of values "spectrum-concentration" will be presented in the form of a matrix X (with dimensions $i \times j$), where each row corresponds to the spectrum (the set of frequencies) at a fixed concentration. The determination of the optimum frequency regions was performed using the following procedure:

1) Hypothetical spectrum of an "ideal binary solution" was injected into consideration. Such liquid consists of molecules of types A and B, and they do not interact with each other during the mixing (complexes are not formed). The corresponding model matrix for the idealized binary solution is X_{mod}, and the spectra of pure components A and B are I_A and I_B, respectively.

2) The model matrix X_{mod} (matrix of the ideal solution) is calculated as a linear combination of I_A and I_B:

$$X_{\text{mod}} = 0.01 \begin{pmatrix} I_A N_1 + I_B(1 - N_1) \\ I_A N_2 + I_B(1 - N_2) \\ \dots \\ I_A N_i + I_B(1 - N_i) \end{pmatrix}. \qquad (1)$$

The matrix X of the measured values for the real binary solution is different from the idealized (model) matrix because the interaction between molecules change the vibrational characteristics of the system. The differences between the real and model solutions define the auxiliary matrix:

$$X_{\text{res}} = X - X_{\text{mod}}. \qquad (2)$$

The last matrix contains information about the conditions, under which the differences of shapes and shifts of the resonant frequencies of the vibrational bands caused by the formation of complexes are most clearly manifested. 3) Frequency regions where the matrix X_{res} has a maximum deviations from the zero level can be considered as areas with the greatest manifestation of the intermolecular interactions in the formation of complexes. In the future, it will be a subject of the detailed analysis. The exclusion of spectral regions, where the intermolecular interaction is weak, helps to improve the accuracy of calculations. Information about the number of complexes derived from the analysis of the residual intensity in the matrix X_{res} should complement the results of MCR-ALS analysis.

3.3. Multivariate curve resolution

The resolution methods decompose mathematically a global mixed instrumental response into the pure contributions due to each component in the system [16]. This mixed signal is organized in the matrix X containing the raw information about all the components present in the data set. The resolution methods allow the decomposition of the initial mixture data matrix X into the product of two data matrices C and S^T, each of them including the pure response profiles of the n mixture or process components associated with the row and column directions of the initial data matrix, respectively. In the matrix notation, the expression valid for all resolution methods is as follows:

$$X = CS^T + E, \qquad (3)$$

where $X(i \times j)$ is the original data matrix, $C(i \times n)$ and $S^T(n \times j)$ are the matrices containing the pure response profiles related to the data variation in the row and column directions, respectively, and $E(i \times j)$ is the error matrix, i.e. the residual variation of the data set that is not related to any chemical contribution. The parameters i and j are the numbers of rows and columns of the original data matrix, respectively, and n is the number of chemical components in the mixture or process. C and S^T are often referred to concentration profiles and spectra (hence, their names). The mathematical decomposition of a single data matrix, no matter the method used, is known to be subjected to ambiguities [17]. This means that many sets of paired C and S^T-type matrices can reproduce the original data set with the same fit quality. In other words, the correct reproduction of the original data matrix can be achieved by using the response profiles differing in shape (rotational ambiguity) or in magnitude (intensity ambiguity) from the sought (true) ones [19]. Mathematically, it can be written as follow:

$$X = CS^T = CTT^{-1}S^T = \tilde{C}\tilde{S}^T, \tag{4}$$

where $T(n \times n)$ – invertible matrix. If T is an orthogonal matrix, the ambiguity is called rotational.

The Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) method is a popular chemometric one used for the resolution of multiple component responses in unknown unresolved mixtures. MCR-ALS solves iteratively Eq. (3) by an Alternating Least Squares algorithm which calculates the concentration C and pure spectral S^T matrices optimally fitting the experimental data matrix X. This optimization is carried out for a proposed number of components with the use of the initial estimates of either C or S^T.

4. Results

4.1. Acetone-chloroform

The FTIR transmission spectra of an acetone–chloroform solution (Fig. 1) are registered in the spectral range 4500–3900 cm^{-1}. This spectral range was chosen due to the weak absorption of overtones and composite frequencies in the near-IR region. The weak absorption allows us to use the liquid cell with a relatively large value of the optical beam path (1 mm). Compound vibrations of acetone were determined at 4009 cm^{-1}, 4065 cm^{-1}, 4142 cm^{-1}, 4185 cm^{-1}, 4315 cm^{-1}, 4357 cm^{-1}, 4420 cm^{-1}, and the compound vibration of chloroform was determined at 4213 cm^{-1} ($\nu_1+\nu_4$), where ν_1(≈3033 cm^{-1}) is the frequency of C–H symmetric stretching vibrations of chloroform, and ν_4(≈1220 cm^{-1}) is the frequency of strain C–H vibrations of chloroform [24]. The selection of the spectral range 4500–3900 cm^{-1} was performed due to several reasons. First, the spectral contours of chloroform and acetone overlap slightly in this region, which is best suited for the separation of the complexes with the use of MCR-ALS. Second, the measurements in the mid-IR region require us to use the optical beam path around 10–25 μm. Therefore, this range is not preferred for the quantitative analysis.

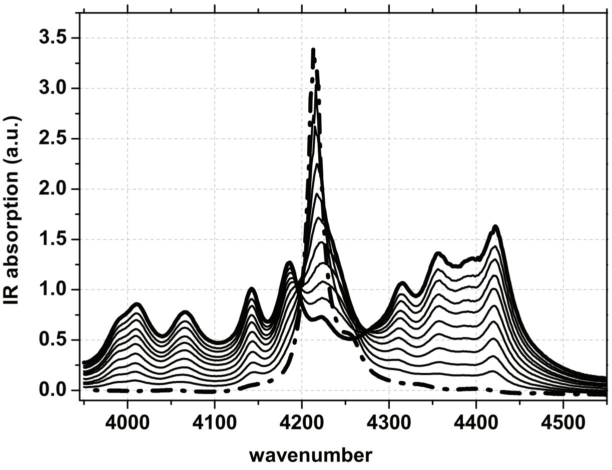

Fig. 1. NIR spectra of an acetone–chloroform solution in the range 4500–3900 cm^{-1}. The solution concentration step is 10 vol.%, continuous line – the spectrum of pure acetone, the dotted line – the spectrum of pure chloroform

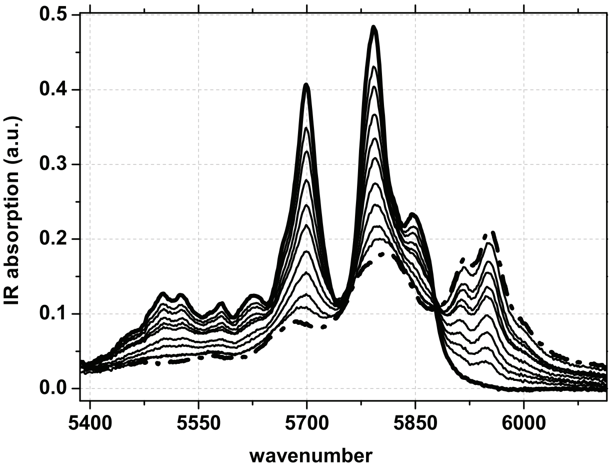

Fig. 2. NIR spectra of an ethyl acetate–cyclohexane solution in the range 6150–5400 cm^{-1}. The solution concentration step is 10 vol.%, continuous line – the spectrum of pure ethyl acetate, the dotted line – the spectrum of pure cyclohexane

4.2. Ethyl acetate–cyclohexane

Figure 2 shows the IR spectra obtained in the transmission mode (in absorbance units) for the

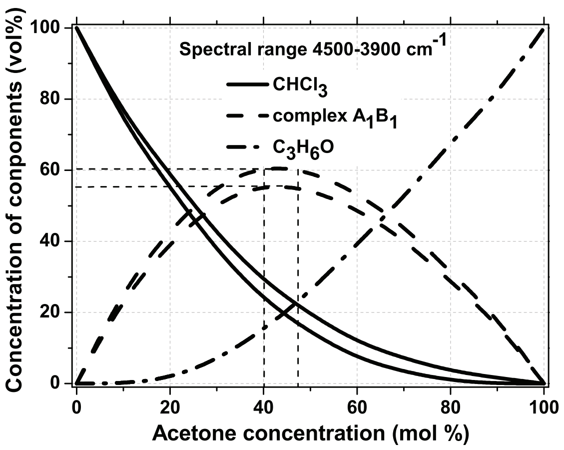

Fig. 3. Minimum and maximum concentration profiles of three components in the acetone–chloroform solution, which are obtained by MCR-ALS analysis of the IR spectra in the region 4500–3900 cm^{-1}. The concentration range between the upper and lower curves of the same type points to the existence of a range of solutions with a given residue

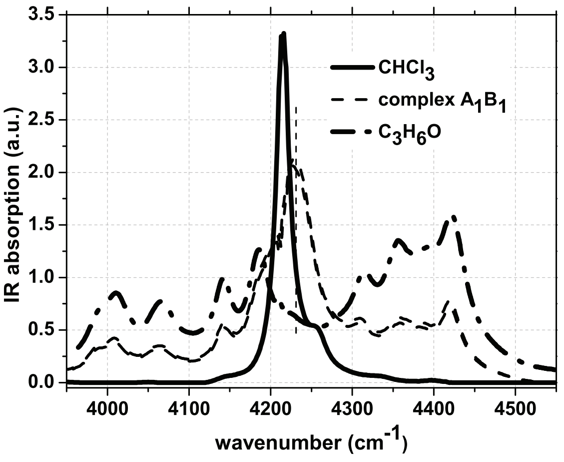

Fig. 4. Minimum and maximum spectra profiles of three components in the acetone–chloroform solution, which are obtained by MCR-ALS analysis of the IR spectra in the region 4500–3900 cm^{-1}. The concentration range between the upper and lower curves of the same type points to the existence of a range of solutions with a given residue

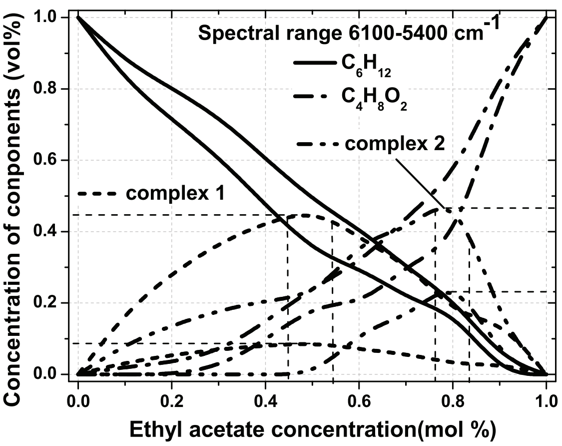

Fig. 5. Minimum and maximum concentration profiles of three components in the ethyl acetate–cyclohexane solution, which are obtained by MCR-ALS analysis of the IR spectra in the region 6100–5400 cm^{-1}. The concentration range between the upper and lower curves of the same type points to the existence of a range of solutions with a given residue

ethyl acetate–cyclohexane solution in the range 6150–5400 cm^{-1}. This range is responsible for the C–H stretching vibrations of cyclohexane and ethyl acetate. A large number of different vibrational modes of ethyl acetate and cyclohexane are located in the range of frequencies 4600–3800 cm^{-1}. The latter fact has a negative impact on the ability of the MCR method to separate the concentration of complexes from the obtained spectra. Therefore, the frequency range 4600–3800 cm^{-1} was not analyzed in this paper.

4.3. Multivariate curve resolution

The decomposition of the matrix X was performed for three components of the acetone–chloroform solution (associates of pure acetone, associates of pure chloroform, and one type of complex). The ALS optimization convergence is achieved when, in two consecutive iterative cycles, the relative differences in standard deviations of the residuals between experimental and ALS calculated data are less than a previously selected value, usually chosen as 0.1%. The iterative process in the MCR-ALS analysis failed to be completed successfully with the established criterion of 0.1% during the decomposition of the matrix of the ethyl acetate–cyclohexane solution for 3 components. But the process was successfully completed by the decomposition into 4 components (associates of pure ethyl acetate, associates of pure cyclohexane, and two types of complexes). The initial approximation for the matrixes C and S^T was determined, by using the evolving factor analysis during the processing of the spectra of the solution [25].

The concentration and spectral profiles of the complexes for the acetone–chloroform solution (Figs. 3 and 4) and for the ethyl acetate–cyclohexane solution (Figs. 5 and 6) were obtained by the method MCR-ALS. The accuracy of the determination of the complexes in a solution (maximum and minimum concentrations and spectral profiles) was evaluated, by using the MCR-bands method [22].

The matrices for the acetone–chloroform solution in the range of 4500–3900 cm^{-1} and for ethyl acetate–cyclohexane solution in the range 6100–5400 cm^{-1} were obtained by the analysis of the residual intensity in spectra. The graphic representation of the matrices is shown in Figs. 7 and 8.

There is only one extreme in the acetone–chloroform solution, as is seen in Fig. 7. This confirms the feasibility of selecting the ternary system (two pure substances and one type of complexes) in MCR-ALS analysis. Figure 8 shows the presence of two concentration extrema in the ethyl acetate–cyclohexane solution. This correlates well with the fact that (as mentioned above) the selection of only one complex in a solution (decomposition into 3 main components) gives no satisfactory results in the MCR-ALS analysis. The convergence of the iterative process could be achieved only by introducing two complexes (four-component model) during the MCR-ALS analysis.

The concentration of complexes in the acetone–chloroform solution (Fig. 3) obtained by analyzing the spectral range 4500–3900 cm^{-1} reaches a maximum at a molar content of acetone of 44±4% (X-axis in Fig. 3). The maximum value corresponds to a molar concentration of complexes of 58 ± 2% of the total concentration of the components in the binary solution (Y-axis in Fig. 3).

Two types of complexes in the ethyl acetate–cyclohexane solution, which are obtained by analyzing the spectral range 6100–5400 cm^{-1} (Fig. 5), have the following characteristics:

1) The concentration of the type-I complexes reaches a maximum, when the content of ethyl acetate is 50 ± 5 mol.%, and the value of maximum concentration is 27 ± 18 mol.%;

2) The concentration of the type-II complexes reaches a maximum, when the content of ethyl acetate is 80 ± 5 mol.%, and the value of maximum concentration is 34 ± 12 mol.%.

The large ambiguity in the concentrations of complexes in the ethyl acetate–cyclohexane solution is

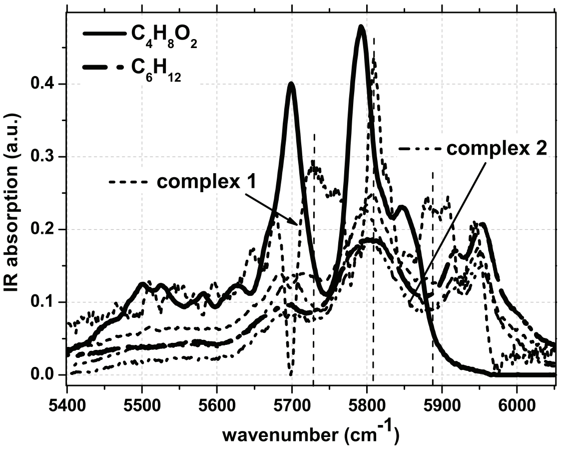

Fig. 6. Minimum and maximum spectra profiles of three components in the ethyl acetate–cyclohexane solution, which are obtained by MCR-ALS analysis of the IR spectra in the region 6100–5400 cm^{-1}. The concentration range between the upper and lower curves of the same type points to the existence of a range of solutions with a given residue

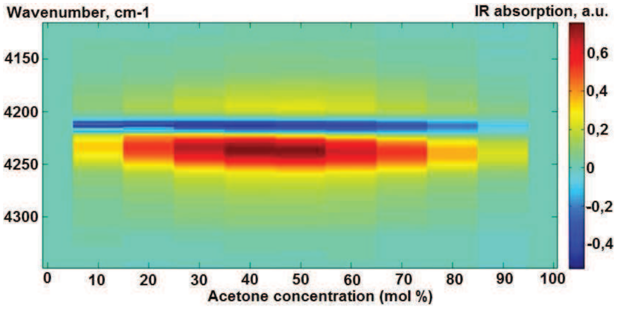

Fig. 7. Graphic representation of the residual intensity in the IR spectra for the acetone–chloroform solution in the range 4500–3900 cm^{-1}

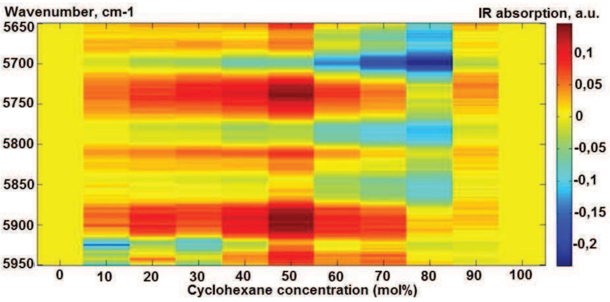

Fig. 8. Graphic representation of the residual intensity in the IR spectra for the ethyl acetate–cyclohexane solution in the range of 6100–5400 cm^{-1}

associated with significantly lower forces of intermolecular interaction between molecules A and B in comparison with those in the acetone–chloroform solution. The stoichiometry of complexes in the ethyl acetate–cyclohexane solution was calculated according to the concentration profiles (Fig. 5). The complex has a composition close to $[A_1B_1]$ (A – acetone, B – chloroform) in the chloroform-acetone solution. The type-I complex has a composition close to $[X_1Y_1]$ (X – ethyl acetate, Y – cyclohexane) and the type-II complex has a composition close to $[X_5Y_1]$ in the ethyl acetate–cyclohexane solution.

The extremum in Fig. 7 is located in the spectral region 4250–4220 cm^{-1} at an acetone concentration of 44 ± 4 mol.% in the acetone–chloroform solution. The extrema in Fig. 8 are located in the spectral regions 5750–5720 cm^{-1}, 5820–5800 cm^{-1}, 5910–5880 cm^{-1} at the concentrations of ethyl acetate 50 ± 5 and 80 ± 5 mol.%. These data are consistent with results obtained by MCR-ALS analysis of the measured solutions (Fig. 4, 6). Information about the number of complexes in solutions obtained by the analysis of the residual intensity in the matrix X_{res} correlates with the MCR-ALS data. This indicates that the data from the spectra of the 3-rd and 4-th main components obtained by the MCR-ALS analysis (which are interpreted as complexes) are actually derived from the presence of the concentration extrema in the matrix X_{res} (Figs. 7 and 8).

5. Conclusions

The experimental results confirm the possibility to describe the structure of a liquid acetone–chloroform solution as the combination of three components: free acetone, free chloroform, and complexes $[A_1B_1]$, consisting of both types of molecules.

It is shown that the ethyl acetate–cyclohexane solution can be regarded as a set of four components: free ethyl acetate, free cyclohexane, and complexes $[X_1Y_1]$ and $[X_5Y_1]$ consisting of both types of molecules. The ambiguity in determining the concentration of complexes in the ethyl acetate–cyclohexane solution is more than in the acetone–chloroform solution. This is due to the fact that the conditions of successful MCR-ALS analysis hold to a less extent for ethyl acetate–cyclohexane solution. These are the absence of strong intermolecular interactions in the complexes (hydrogen bonds are not formed) and the overlap of the spectral lines of ethyl acetate and cyclohexane.

An auxiliary method for determining the number of complexes by analyzing the residual intensity in the IR spectra is proposed. Minima/maxima of absorption in the residual intensity matrix X_{res} coincide with those in the concentration of complexes in the matrix of concentration profiles obtained by MCR-ALS. This indicates that the data from the spectra of the main components obtained during MCR-ALS analysis are actually derived from the presence of concentration extrema in the matrix X_{res}.

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О.О. Ільченко, В.В. Ніконова,
А.М. Куцик, В.В. Обуховський

КІЛЬКІСНИЙ АНАЛІЗ КОМПЛЕКСОУТВОРЕННЯ В МОЛЕКУЛЯРНИХ РОЗЧИНАХ АЦЕТОН–ХЛОРОФОРМ І ЕТИЛАЦЕТАТ–ЦИКЛОГЕКСАН

Резюме

Реальні бінарні (подвійні) розчини "ацетон–хлороформ" і "етилацетат–циклогексан" моделюються ідеальними багатокомпонентними (потрійними, четверними) сумішами, які складаються з асоціатів типу $[A_p]$, $[B_q]$ і комплексів $[A_nB_m]$. Спектри поглинання цих розчинів в ближньому ІЧ діапазоні аналізуються з використанням хемометричного методу MCR-ALS. В розчині ацетон–хлороформ зафіксовано утворення комплексу одного типу $[A_1B_1]$, а в розчині етилацетат–циклогексан знайдено два комплекси типів $[X_1Y_1]$ і $[X_5Y_1]$. Запропоновано допоміжний метод визначення кількості комплексів шляхом аналізу залишкової інтенсивності в ІЧ спектрах. Інформація про кількість комплексів у розчині, що отримана під час аналізу залишкової інтенсивності, корелює з даними MCR-ALS і використовувалась для інтерпретації процесів комплексоутворення в бінарних розчинах.