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# Vapor–Liquid Equilibrium in Binary and Ternary Azeotropic Solutions Acetonitrile-Ethanol-Water with the Addition of Amino Esters of Boric Acid

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**Abstract:** The effect of amino esters of boric acid (AEBA) on the conditions of vapor–liquid equilibrium in binary mixtures of acetonitrile–water, ethanol–acetonitrile and a three-component mixture of ethanol-acetonitrile-water was investigated. Residual curves and vapor–liquid phase equilibrium conditions (TPXY data) were experimentally measured at atmospheric pressure for a binary mixture of acetonitrile-AEBA and a triple mixture of acetonitrile-water-AEBA. Previously unknown energy binary parameters of groups B, $CH_2N$ with group $CH_3CN$ were determined for the UNIFAC model. The correction of the value of the binary parameter water—acetonitrile was carried out. On the basis of thermodynamic modeling, the degree of influence of AEBA on the relative volatility of acetonitrile in binary and ternary mixtures was analyzed. It is shown that the use of AEBA removes all azeotropic points in the studied mixtures. In this case, acetonitrile turns out to be a volatile component, and water is a non-volatile component in the entire concentration range.

**Keywords:** vapor–liquid equilibrium; azeotropic mixtures; UNIFAC model; extractive distillation

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## 1. Introduction

Acetonitrile and ethanol are important organic solvents that are used in many industries [1,2]. The areas of their use are quite wide and include components for chemical synthesis, solvents, entrainers, etc. For example, ethanol is an important source in the synthesis of esters, is used as a solvent for the production of paints and varnishes, for the manufacture of medicines, food, consumables in household chemicals and is one of the most common types of biofuels. [3]. Acetonitrile is necessary for the production of pharmaceuticals, purification of butadiene and fatty acids [4,5], as a medium for chemical reactions, where it can also serve as a catalyst [6].

In industrial technologies, acetonitrile and ethanol are often present in mixtures with water [7–9]. Since acetonitrile and ethanol are often used as mobile phases in liquid chromatography, a ternary mixture of ethanol-acetonitrile-water is formed at the final stage of the analytical process, requiring separation. This raises the problem of separating these mixtures into individual substances. The separation of acetonitrile and ethanol from their liquid solutions in water by using distillation is difficult due to the formation of both binary and ternary azeotropic mixtures by them [10–12]. Thus, the acetonitrile–water system forms an azeotrope boiling at 349.65 K and containing 83.7 wt.% acetonitrile [13]; the ethanol–acetonitrile system forms an azeotrope boiling at 345.65 K and containing 46.9 wt.% acetonitrile [13]; the ethanol–water system forms an azeotrope boiling at 351.35 K and containing 96 wt.% ethanol [13]; the ethanol-acetonitrile-water system forms a ternary azeotropic mixture boiling at 346.05 K and containing 55 wt.% ethanol, 44 wt.% acetonitrile [10]. From the point of view of ecology and economic benefits, the problem of separating such ternary systems is extremely important [14].

To separate azeotropic mixtures of acetonitrile and ethanol with water, methods such as azeotropic distillation [15–17], pressure distillation [18], extractive distillation [19–25], extraction [26,27], pervaporation [28–33] and adsorption [34,35]. At the same time, one of the most effective industrial methods for separating azeotropic mixtures of acetonitrile and ethanol with water is extractive distillation. In this case, an entrainer is added to the azeotropic mixture, which leads to an increase in the relative volatility of the components of the mixture being separated [36–38]. Solvents such as dimethyl sulfoxide [39], ethylene glycol [39–42], glycerol [41,43,44], butyl acetate [45,46], and eutectic mixtures [47] are used as entrainers. However, their use is hampered by the high dosage requirements of these compounds and by the problems of mixing with a solution of acetonitrile in water. Butyl acetate is highly volatile and can contaminate the distillate.

Recently, ionic liquids (ILs), which have such unique properties as low saturated vapor pressure and a high degree of influence on the relative volatility of the components of azeotropic mixtures, have been considered as entrainers. The high cost of ionic liquids compared to conventionally used substances makes it difficult to use them as industrial entrainers [48].

The papers [49,50] presented the results of studying the properties of amino esters of boric acid (AEBA) synthesized using boric acid, triethanolamine, and various glycols and triols (Figure 1).

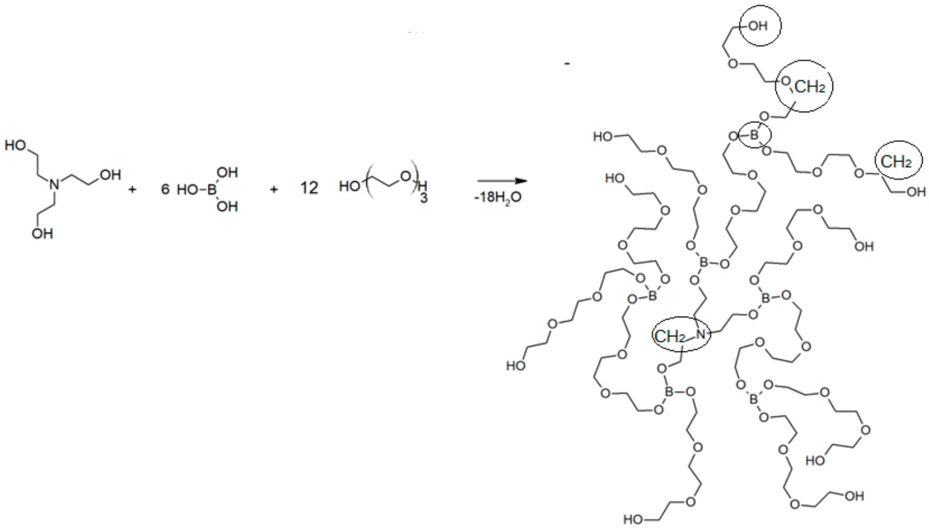

**Figure 1.** Scheme for the synthesis of AEBA–TEG.

In this article, glycols and triols used in the synthesis of AEBA are referred to as AEBA-MEG (monoethylene glycol), AEBA-DEG (diethylene glycol), AEBA–TEG (triethylene glycol), AEBA-GL (glycerol).

It was shown [49,50] that AEBA–TEG/DEG exhibit the properties of an ionic liquid. The melting point of AEBA–TEG/DEG is below 100 °C, AEBA have high electrical conductivity of aqueous solutions and extremely low saturation vapor pressure. The advantage of AEBA-MEG/TEG/DEG/GL in comparison with ILs is the ease of synthesis and the availability of the reagents used for the synthesis. The studies carried out in [49,50] showed the promise of using AEBA–TEG/DEG for the extractive distillation of an ethanol–water mixture. The purpose of this work is to carry out further studies of AEBA as highly effective entrainers for the separation of azeotropic mixtures of acetonitrile–water and acetonitrile-ethanol-water. All experimental studies in this work were carried out using AEBA–TEG. Based on the obtained TPXY data, the parameters of the UNIFAC model were determined, which made it possible to simulate the conditions of vapor–liquid equilibrium in acetonitrile-ethanol-water solutions in the presence of AEBA synthesized from various glycols and triols.

## 2. Experimental Part

### 2.1. Synthesis of Amino Esters of Boric Acid

When obtaining amino esters of boric acid, triethylene glycol was used as the glycol component. The synthesis was carried out in one step. Triethanolamine, boric acid, and triethylene glycol were introduced into a three-necked round-bottomed flask at a molar ratio of [TEA]:[$H_3BO_3$]:[TEG] = 1:6:12. This molar ratio of the reagents used was found to be optimal in previous work [49]. The calculated amount of boric acid (6 mol) was 2.793 g, triethanolamine (1 mol) was introduced 1.124 g, triethylene glycol (12 mol) was used in the amount of 9.644 g/13.485 g, respectively. The temperature of the reaction system was brought to 93 °C, and then at a residual pressure of 10 mmHg the synthesis was carried out for 2 h. Stirring was carried out by bubbling the reaction system with water, which was released during the reaction. The chosen synthesis conditions are necessary to maintain the content of residual water, which is a component of the AEBA structural organization. The course of the reaction was monitored after reaching the required amount of hydroxyl groups, determined titrimetrically. The water content in the synthesized AEBA–TEG was determined using a Mettler Toledo V20 volumetric titrator (Zürich, Switzerland) according to the Karl Fischer method and was 0.63 wt.%.

#### Materials

Triethylene glycol produced by PJSC Nizhnekamskneftekhim (Nizhnekamsk, Russia) was used. Triethanolamine produced by OJSC Kazanorgsintez (Kazan, Russia). Boric acid (99.99%) was purchased from Sigma-Aldrich. The triethylene glycol was further dried to a residual moisture content of less than 0.01% wt.%.

To carry out distillation experiments, ethanol with a purity of 96.3 wt.% and acetonitrile (99.99%) produced by EKOS-1 OJSC (Moscow, Russia) were used.

Deionized water prepared at the Osmodemiya 12 plant (IDROTECNICA s.r.I., Genova GE, Italy) was used to obtain aqueous solutions.

### 2.2. Experimental Methods for Studying Phase Equilibrium

To assess the effect of AEBA on the relative volatility of acetonitrile in aqueous solutions, data on the vapor–liquid phase equilibrium in the three-component system acetonitrile-water-AEBA are needed. Since such data are not available, in this work they were obtained on the basis of experimental measurements. Two methods were used to experimentally study the equilibrium conditions of vapor–liquid: the method of open evaporation and the method of measurement on an ebulliometer of the Swietoslavsky type. The method of open evaporation is less laborious and rather quickly allows one to qualitatively and quantitatively evaluate the effect of adding solvents on the conditions of phase equilibrium in an azeotropic mixture in a certain concentration range [51]. If this method showed the necessary degree of influence on the relative volatility of the mixture components, the conditions of vapor–liquid equilibrium were studied on an ebulliometer for a specific concentration composition.

#### 2.2.1. Method of Open Evaporation

An IKA-RV 10 rotary evaporator (IKA, Staufen im Breisgau, Germany) was used to conduct experimental studies of vapor–liquid phase equilibrium using the method of open evaporation (shown in Figure 2).

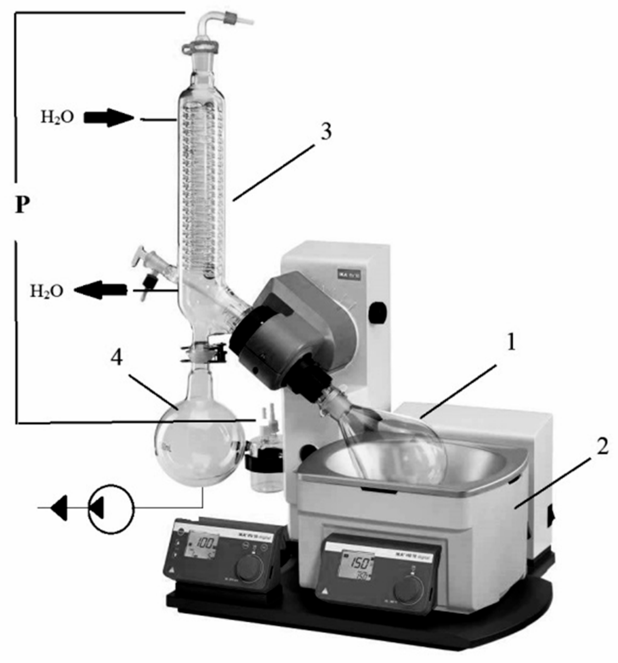

**Figure 2.** Scheme of the rotary evaporator IKA-RV 10 digital: 1—evaporator cube, 2—oil bath, 3—refrigerator, 4—receiving flask.

A mixture of a known composition to be separated in an amount of approximately 200 g was placed in an evaporator cube. Heat for heating came from an electric heater through a layer of oil. The oil temperature was maintained at 10–20 K above the boiling point of the mixture in the cube. The vapors formed during the boiling process condensed in the condenser, and then the condensate entered the receiving flask. The distillation process was carried out until no more than 1/10 of the initial amount of the volatile fraction remained in the cube. During the evaporation process, 6–8 samples of distillate were taken in the amount of 10–20 g each. The mass of the total amount of the selected distillate and the mass of the bottom residue were checked for compliance with the material balance in which the discrepancy did not exceed 1.5 wt.%.

Based on the experimental data obtained, residual curves were calculated, i.e., the dependence of the composition of the mixture in the cube on the amount of distillate removed:

$$x_{i+1} = (L_i x_i - P_{i+1} y_{i+1})/(L_i - P_{i+1}),\ i = 0 \ldots n - 1 \quad (1)$$

$$L_{i+1} = L_i - P_{i+1}, \quad (2)$$

where $P_i$ and $y_i$,—mass and composition of the i-th portion of the distillate; $L_i$ and $x_i$ mass and composition boiling mixture after carried out i-th portion of the distillate; n is the number of distillate samples taken, $L_0$ is the initial amount of the mixture, x and L were taken to be the concentration of the volatile component in the mixture and the mass of the boiling mixture, excluding the entrainer.

### 2.2.2. Study of Phase Equilibrium on the Swietoslavsky Ebulliometer

To measure the compositions of the equilibrium vapor and liquid phases, we used the Swietoslavsky ebulliometer [52] (PJSC Khimlaborpribor, Klin, Russia). The installation diagram is shown in Figure 3.

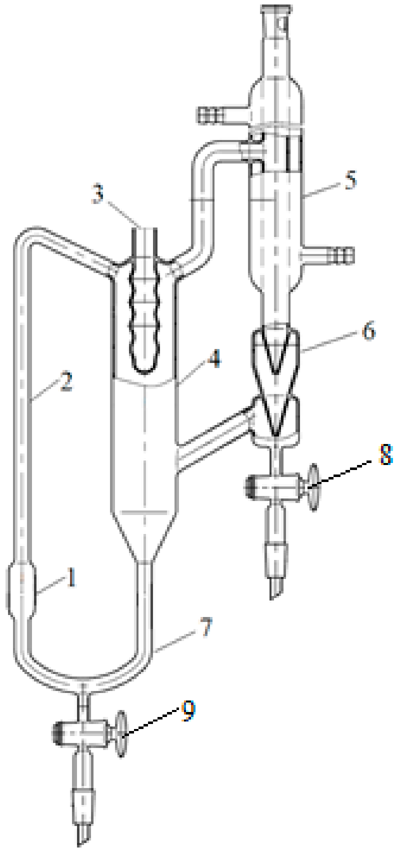

**Figure 3.** Swietoslavsky ebuliometer: 1—cube; 2—Cottrell pump; 3—pocket for a thermometer; 4—separation space; 5—refrigerator; 6—drop counter; 7—overflow tube; 8,9—distillate and cube sampling valve.

An LT-300-N electronic thermometer (Termeks LLC, Tomsk, Russia) with an error of ±0.05 K was used to measure the temperature and installed in sleeve 3 filled with electrocorundum.

Cube 1 was filled with the studied mixture through refrigerator 5. Then, the mixture was heated with a flexible electric heater installed on the outer surface of cube 1. The mixture was heated to boiling and kept for 2.5 h to establish equilibrium in the system. The boiling point did not change for 2.5 h. At the same time, samples of the vapor phase condensate were taken to clarify the composition of the distillate 6 and samples of the liquid phase were taken to clarify the composition of the boiling mixture from the bottom of the overflow tube 7.

The reliability of the results obtained on the Swietoslavsky ebulliometer was verified by comparing the measured phase equilibrium conditions for the acetonitrile–water binary system at an atmospheric pressure of 760 mmHg with the experimental results of other authors [53,54]. The comparison results are shown in Figures 4 and 5. The discrepancy in vapor concentration was 2 wt.%, at a boiling point of 1.3%, which confirms the reliability of the experimental measurement technique used.

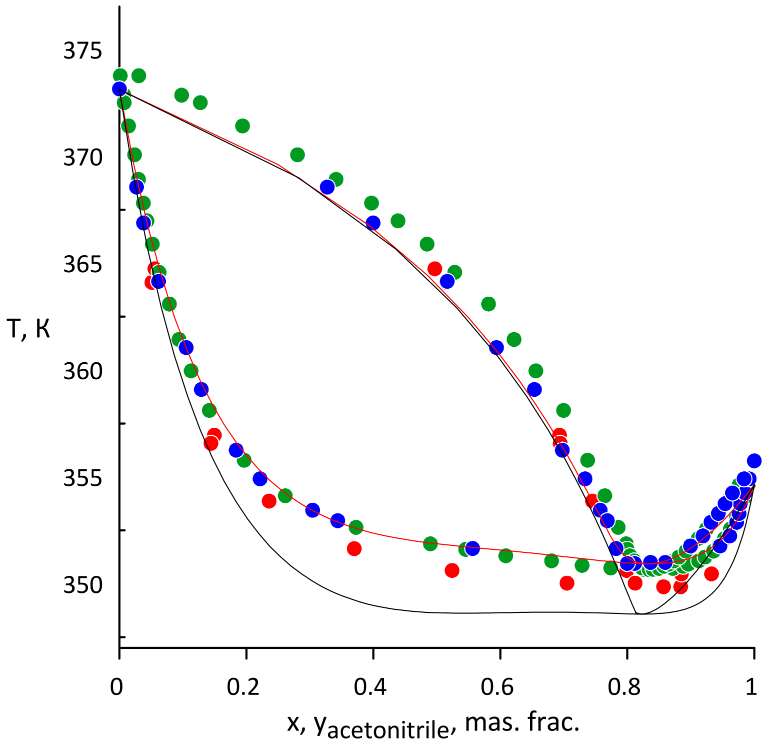

**Figure 4.** TXY diagram for a binary mixture of acetonitrile–water at atmospheric pressure. Green circles—[53], blue circles—[54], red circles—experimental data, red line—calculated by the UNIFAC model with corrected parameters black line—calculated by the UNIFAC model [55].

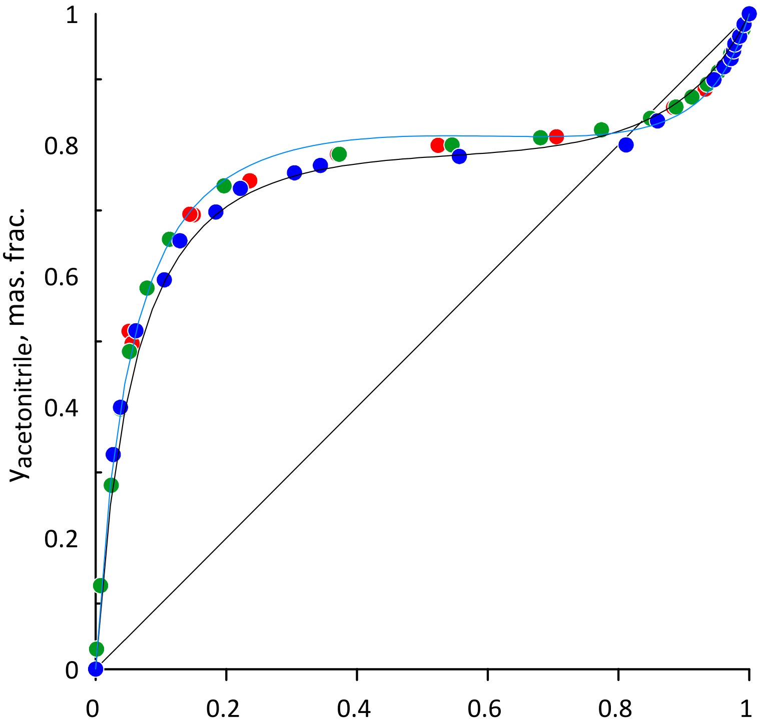

**Figure 5.** YX diagram for a binary mixture of acetonitrile–water at atmospheric pressure. Green circles—[53], blue circles—[54], red circles—experimental data, black line—calculated by the UNIFAC model with corrected parameters, blue line—calculated by the UNIFAC model [55].

### 2.2.3. Simulation of Vapor–Liquid Phase Equilibrium Conditions

When designing technological distillation processes using entrainers of various molecular structures, reliable models are needed to calculate the conditions for vapor–liquid phase equilibrium. Under conditions of low pressure, the relationship between the equilibrium concentrations of component i in the vapor $y_i$ and liquid phases xi is determined by the following relationship:

$$y_i = (x_i \cdot \gamma_i \cdot P_i{}^S(T))/P, \quad (3)$$

here $\gamma_i$ is the activity coefficient; $P_i{}^S$-saturated vapor pressure of the pure component i; P is the pressure in the system. The main difficulty in expression (4) is the calculation of activity coefficients. For the systems studied in this work, a promising method for describing the activity coefficient is the method of group components UNIFAC (UNIquac Functional-group Activity Coefficients) [55]. The UNIFAC method is based on the concept of group contribution, i.e., the interaction between two molecules is represented as interactions between atoms or groups of atoms that make up the molecule. It is assumed that the characteristics of the intergroup interaction will not strongly depend on whether the groups belong to different molecules, i.e., from their atomic environment in the molecule. Despite the fact that this assumption is not always true, the number of parameters required to describe the activity coefficients of various substances and their mixtures turns out to be incommensurably less than the number of substances. In addition, an important advantage of the UNIFAC model is its predictive ability in the absence of any experimental data if the substances included in the system under consideration consist of atoms (groups) whose interaction parameters are known.

To use the model of group components, it is necessary to divide the molecules of the components of the simulated mixture into functional groups as, for example, was done for water and alcohols [57]. The AEBA–TEG molecule is proposed to be divided into the following groups (Figure 1): 6—B is a boron group, 35—$CH_2$ is an alkane group, 42—$OCH_2$ is an ether group, 1—$NCH_2$ is an amino group, and 9—OH is an alcohol group [50].

The data on the parameters of the interaction of the $CH_2$, $OCH_2$, $CH_2N$, OH, and $H_2O$ groups with the B group that are not available in the literature were previously determined in [33]. In this work, according to the obtained experimental data, the parameters of the interaction of the CCN group (in the composition of acetonitrile) with the boron group B and the amino group $CH_2N$, which are absent in the literature, were determined. We did not find UNIFAC parameter values for these groups either in the literature [56,57] on group interaction parameters or in the complete database presented in the Dortmund Data Bank (DDB) [58].

Obviously, the use of the UNIFAC model to describe the conditions of vapor–liquid equilibrium is especially effective for AEBA solutions, since AEBA molecules synthesized on the basis of various glycols will differ only by a certain number of functional groups. This makes it possible to predictively model the effect of AEBA of various structures on the relative volatility of the components of the mixture under consideration.

The activity coefficients in the UNIFAC model are presented as:

$$\ln\gamma_i = \ln\gamma_i{}^C + \ln\gamma_i{}^R \quad (4)$$

In this case, the activity coefficient is the sum of the combinatorial and residual term. The combinatorial term is determined from the data on the group volume R and the group surface Q, which in turn depend on the van der Waals group volume $V_{\omega k}$ and the surface area $A_{\omega k}$ [57,59]:

$$R_k = V_{\omega k}/15.17, \quad (5)$$

$$Q_k = A_{\omega k}/2.5 \times 10^9, \quad (6)$$

The values $R_k = 0.9371$, $Q_k = 0.9809$ for the boron group B were taken as in [50], for the other groups the values of the geometric parameters are standard [60].

The residual part of the activity coefficient characterizes the interaction energy of groups n and m and is defined as:

$$\psi_{mn} = \exp(-a_{mn}/T), \tag{7}$$

where $a_{mn}$—group interaction parameter.

For each interaction between groups n and m, two parameters $a_{mn}$ and $a_{nm}$ are used.

### *2.3. Methods and Equipment for Measuring Compositions*

The preparation of the initial mixtures and the determination of the mass of the distillate samples taken during the experiment were carried out on a ShincoADJ balance (Tokyo, Japan) with a measurement error of ±0.0001 g.

The water content in the initial reagents and in the selected samples of the distillate was determined on a MettlerToledo V20 Compact Karl Fischer Volumetric volumetric titrator ("Mettler-Toledo AG", Greifensee, Switzeriand) according to the Karl Fischer method (with a relative measurement error of ±3%).

The component composition of the mixture was determined by using Chromatec-Crystal 5000 gas chromatograph (CJSC SKB Khromatek, Yoshkar-Ola, Russia) with a thermal conductivity detector. During the research, a capillary column ZB-FFAP 50 × 0.32 × 0.50 was used in the temperature control mode 348.15 K, the carrier gas was helium and the detector temperature was 493.15 K.

## 3. Results and Discussion

All results presented in this section were obtained under conditions of atmospheric pressure P = 760 mmHg. Experimental studies of the degree of influence of AEBA on the equilibrium of vapor–liquid of binary and three-component solutions acetonitrile-ethanol-water were carried out using AEBA–TEG. Recently [49,50], it was experimentally shown that the fugasity of AEBA compared to water and ethanol can be neglected. Therefore, the absence of AEBA in the vapor phase was assumed here. The objectives of the research included experimental confirmation of the effect of AEBA–TEG on the relative volatility of the components of the mixtures under consideration and obtaining a sufficient amount of experimental data on the conditions of vapor–liquid phase equilibrium (TPXY data) that make it possible to determine adequate values of the unknown energy parameters of the CCN nitrile group with the boron group B and the amino group $CH_2N$. It was shown in [50] that experimental data obtained for AEBA with one type of glycol, for example, AEBA–TEG, are sufficient to determine the parameters of the UNIFAC model. These parameters will provide a satisfactory accuracy in the calculation of phase equilibrium in the systems under consideration when replacing AEBA–TEG with AEBA obtained using other glycols. This is explained by the fact that AEBA molecules synthesized using different glycols will differ only by a certain number of similar groups.

### *3.1. Acetonitrile–Water*

Based on the method of open evaporation, the effect of AEBA–TEG on the relative volatility of acetonitrile in an aqueous solution was evaluated. Figure 6 shows the lines of residual curves obtained for a mixture of acetonitrile–water with the addition of AEBA–TEG in an amount of 20, 40, and 60 wt.%.

The relative volatility of acetonitrile increases with the addition of AEBA, which leads to its faster depletion at the bottom. The change in the behavior of open pairing lines is associated with the disappearance of the azeotropic point of an aqueous solution of acetonitrile in the presence of AEBA.

A detailed measurement of the conditions of phase equilibrium of vapor–liquid in the three-component system acetonitrile-water-AEBA–TEG was carried out on an ebulliometer. The experiment was carried out for three concentrations of AEBA–TEG (20, 40, and 60 wt.%). For each of these concentrations, about 10 points were measured with different acetonitrile/water ratios. The results of the experiments are shown in Figure 7 and in tabular form (Table 1). It follows from Figure 7 that the addition of AEBA–TEG to the acetonitrile–water system increases the concentration of acetonitrile in the vapor phase. The azeotropic point disappears when the content of AEBA–TEG is between 20 and 40 wt.%.

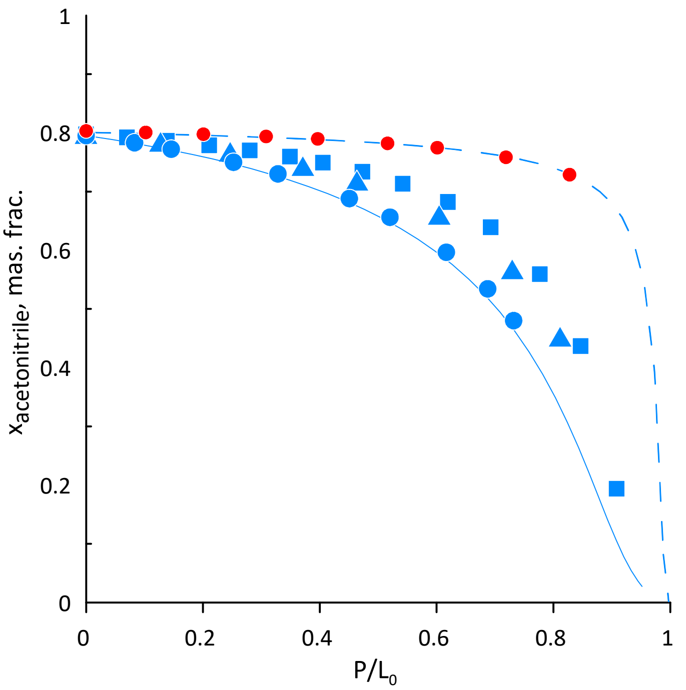

**Figure 6.** Residual curves for a mixture of acetonitrile-water-AEBC-TEG, geometric figures—experimental data, calculation lines according to the UNIFAC model with corrected parameters. AEBA–TEG concentrations: red circles, dotted line—0 wt.%, square—20 wt.%, triangle—40 wt.%, circle, continuous line—60 wt.%.

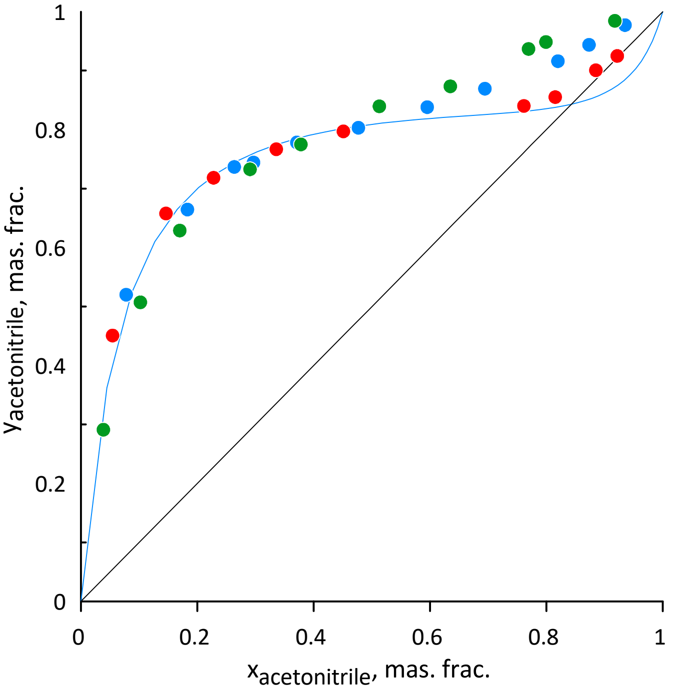

**Figure 7.** Equilibrium of vapor–liquid in the system acetonitrile-water-AEBA–TEG. The line is a binary mixture, geometric figures with the addition of AEBA–TEG (red circles—20 wt.%, blue circles—40 wt.%, green circles—60 wt.%).

**Table 1.** Experimental TPXY data on vapor–liquid equilibrium for an acetonitrile–water mixture in the presence of AEBA–TEG at various concentrations.

| T, K | $w_{AEBA–TEG}$ (Exactly) | $x_{acetonitril}$ | $y_{acetonitril}$ |
|---|---|---|---|
| | AEBA–TEG 0.2 mas. frac. (approximately) | | |
| 367.36 | 0.222 | 0.054 | 0.451 |
| 360.9 | 0.224 | 0.146 | 0.658 |
| 356.8 | 0.228 | 0.228 | 0.718 |
| 354.22 | 0.217 | 0.336 | 0.767 |
| 352.99 | 0.223 | 0.451 | 0.797 |
| 350.8 | 0.216 | 0.761 | 0.840 |
| 352.65 | 0.229 | 0.815 | 0.855 |
| 350.48 | 0.223 | 0.885 | 0.901 |
| 353.73 | 0.231 | 0.922 | 0.925 |
| | AEBA–TEG 0.4 mas. frac. (approximately) | | |
| 368.21 | 0.433 | 0.078 | 0.52 |
| 362.91 | 0.42 | 0.183 | 0.664 |
| 358.94 | 0.432 | 0.264 | 0.737 |
| 359.47 | 0.439 | 0.296 | 0.744 |
| 356.85 | 0.443 | 0.371 | 0.778 |
| 355.26 | 0.434 | 0.477 | 0.803 |
| 354.72 | 0.435 | 0.595 | 0.838 |
| 354.79 | 0.445 | 0.694 | 0.869 |
| 355.24 | 0.432 | 0.82 | 0.916 |
| 356.14 | 0.439 | 0.873 | 0.944 |
| 357.29 | 0.437 | 0.935 | 0.977 |
| | AEBA–TEG 0.6 mas. frac. (approximately) | | |
| 380.25 | 0.661 | 0.038 | 0.291 |
| 374.73 | 0.644 | 0.102 | 0.507 |
| 370.86 | 0.637 | 0.170 | 0.629 |
| 366.95 | 0.644 | 0.291 | 0.733 |
| 363.99 | 0.636 | 0.378 | 0.775 |
| 363.06 | 0.647 | 0.513 | 0.840 |
| 362.06 | 0.630 | 0.635 | 0.873 |
| 361.7 | 0.634 | 0.769 | 0.937 |
| 362.32 | 0.654 | 0.799 | 0.949 |
| 361.71 | 0.639 | 0.918 | 0.984 |

Based on the experimental TPXY data (Table 1), the UNIFAC energy parameters of the interaction of the B, $CH_2N$ groups with the $CH_3CN$ group were determined. These parameters reflect the intermolecular interaction of acetonitrile with AEBA–TEG. For their correct determination from TPXY data for a three-component mixture, it is necessary that the UNIFAC model adequately describes the phase equilibrium in binary solutions of ethanol–water and acetonitrile–water. Satisfactory accuracy of description of TPXY data for the ethanol–water system was shown in [50]. Here, the accuracy of the description by the UNIFAC TPXY model of data for a binary mixture of acetonitrile–water with the literature parameters was tested [55]. Figures 4 and 5 compare the calculation results for YX and TYX diagrams with experimental data [53,54]. It can be seen that the discrepancy, especially in temperature and in the coordinates of the azeotropic point, is significant. Therefore, according to the experimental data from [53,54] and the present work, the parameters of the UNIFAC model were corrected. The obtained parameters for the acetonitrile group with water are shown in Table 2, and the results of calculating the equilibrium conditions are presented in Figures 4 and 5. The corrected parameters increase the accuracy of the description of TPXY data, in particular the temperature value and the coordinates of the azeotropic point.

**Table 2.** Energy parameters of group interaction.

| Group-m | Group-n | $a_{mn}$ | $a_{nm}$ |
|---|---|---|---|
| $H_2O$ | $CH_2$ | 300.00 | 1318.00 |
| $H_2O$ | OH | −229.10 | 353.50 |
| $H_2O$ | $CH_2O$ | 540.50 | −314.70 |
| $H_2O$ | $(C)_3N$ | 304.00 | −598.80 |
| $H_2O$ | B | −237.83 | −1136.35 |
| **$H_2O$** | **CCN** | **186.76** | **79.05** |
| $CH_2$ | OH | 986.50 | 156.40 |
| $CH_2$ | $CH_2O$ | 251.50 | 83.36 |
| $CH_2$ | $(C)_3N$ | 206.60 | −83.98 |
| $CH_2$ | B | 170.60 | −384.58 |
| $CH_2$ | CCN | 597.00 | 24.82 |
| OH | $CH_2O$ | 28.06 | 237.70 |
| OH | $(C)_3N$ | −323.00 | 28.60 |
| OH | B | −281.82 | −722.30 |
| OH | CCN | 6.71 | 185.40 |
| $CH_2O$ | $(C)_3N$ | 5422.00 | −194.10 |
| $CH_2O$ | B | 405.99 | 1825.92 |
| $CH_2O$ | CCN | −18.51 | 38.81 |
| $(C)_3N0$ | B | 113.96 | −13.53 |
| **$(C)_3N$** | **CCN** | **834.46** | **322.39** |
| **B** | **CCN** | **1714.77** | **−66.08** |

Note: Filling and bold font indicate the parameters found corrected in this work.

Also for a binary mixture of acetonitrile–water, the consistency of the residual curves measured by the method of open evaporation with their calculated values was checked. Residual curves were calculated using the equation of open evaporation (Rayleigh equations) of a binary mixture [51]:

$$y\ (x)^* = dx/d\ln(L) + x, \tag{8}$$

where x and L are the composition and mass of the boiling mixture; $y(x)^*$—equilibrium vapor composition, determined by the parameters from Table 2.

The comparison results are shown in Figure 6. Good agreement between the calculated and experimental data is seen.

The minimizing the sum of squared residuals algorithm was used to determine the parameters of interaction between groups B, $CH_2N$ and group $CH_3CN$. The average error according to the equilibrium data was: 3.5% for the concentration of acetonitrile in the vapor, 0.82% for temperature. The used values of the UNIFAC parameters are given in Table 2, where the parameters found and adjusted in the work are highlighted in bold and filled.

Using certain parameters of the UNIFAC model, the consistency of the experimental and calculated residual curves for the acetonitrile-water-AEBA–TEG system was checked. The comparison results for AEBA–TEG are shown in Figure 6, where a satisfactory agreement is seen. The average discrepancy between the experimental and calculated data according to the UNIFAC model for the acetonitrile-water-AEBA system was 4.5%. Figure 8 also compares the calculated and experimental data on the boiling points of the binary mixture of acetonitrile with AEBA–TEG, obtained on the Swietoslavsky ebulliometer. The maximum discrepancy was 1.8%.

The good agreement between the experimental and calculated data shown above makes it possible to use the UNIFAC model with the parameters from Table 2 for predictive modeling of vapor–liquid equilibrium conditions in the systems considered here. Figure 9 shows the effect of AEBA of various molecular structures on the relative volatility of acetonitrile in an aqueous solution.

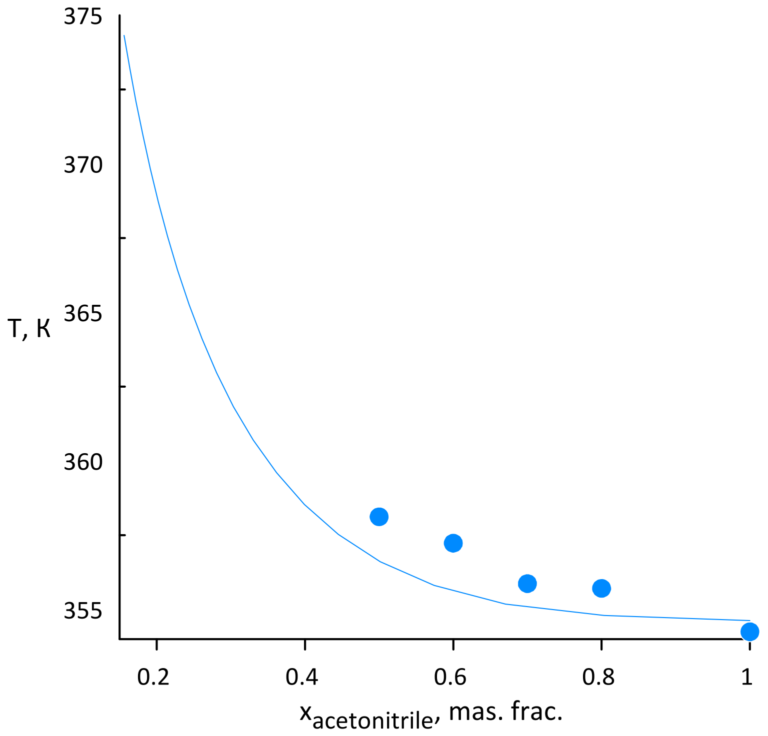

**Figure 8.** Boiling temperature of the binary mixture acetonitrile-AEBA–TEG at atmospheric pressure. Geometric figures—experimental data, line—calculation according to the UNIFAC model (Table 2).

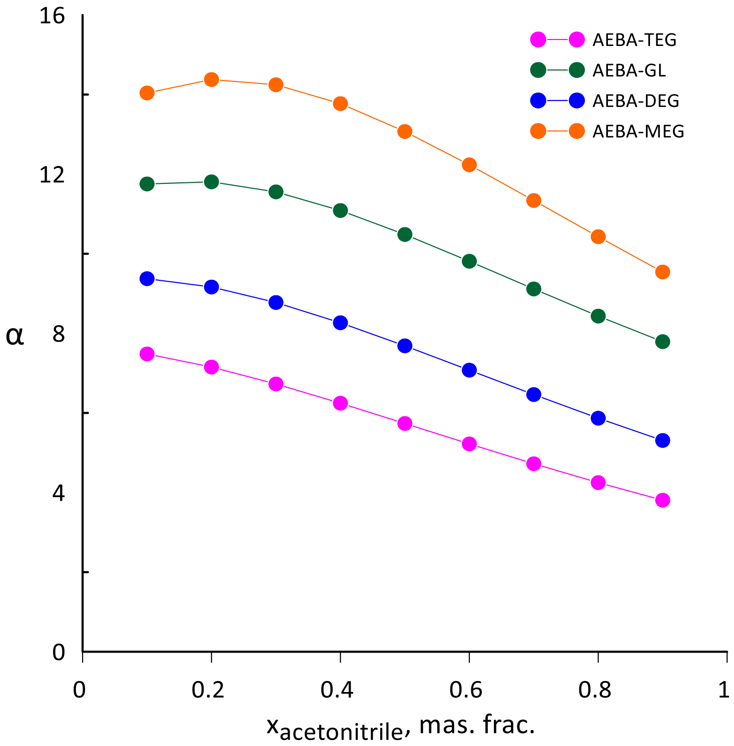

**Figure 9.** Relative volatility of acetonitrile in an azeotropic mixture of acetonitrile–water with the addition of 60 wt.% AEBA-GL/MEG/DEG/TEG.

The relative volatility coefficient of component 1 in solution with component 2 was determined as:

$$\alpha_{12} = (y_1/x_1)/(y_2/x_2), \tag{9}$$

where $y_1$ and $y_2$ are the equilibrium concentration of components 1, 2 in the vapor, $x_1$ and $x_2$ are the concentrations of components 1, 2 in the solution.

It can be seen that an increase in the length of the glycol molecule, which is part of AEBA, reduces the relative volatility of acetonitrile. At the same time, as was shown in [46], with an increase in the length of glycol, the decomposition temperature of AEBA increases. Therefore, when choosing a specific AEBA as an entrainer, these dependencies must be taken into account. Figure 9 also shows that AEBA synthesized using monoethylene glycol (AEBA-MEG) has a high degree of influence on the volatility of acetonitrile.

### *3.2. Ethanol–Acetonitrile*

The effect of AEBA on the relative volatility of the components of an ethanol–acetonitrile mixture was studied in this work. The study was carried out only on the basis of modeling with UNIFAC parameters, from Table 2. The adequacy of the description of the interaction between acetonitrile-AEBA and ethanol-AEBA is confirmed by the data presented above and in [50]. The adequacy of the TPXY description of the ethanol–acetonitrile mixture data for the UNIFAC model is shown in Figures 10 and 11 by comparison with the experimental data from [61].

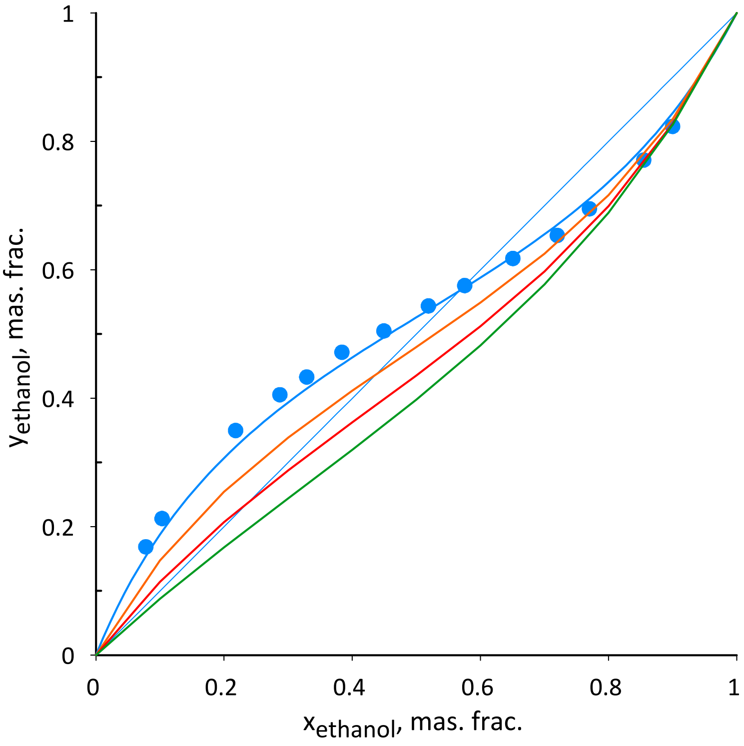

**Figure 10.** Equilibrium compositions of vapor and liquid in the ethanol- acetonitrile-AEBA–TEG system. The lines are the calculation according to the UNIFAC model (Table 2), the dots are the experimental data from [61]. AEBA–TEG concentration: points, blue line—0 wt.%, yellow line—20 wt.%, red line—40 wt.%, green line—60 wt.%.

Figure 10 shows the results of modeling the effect of AEBA–TEG on the vapor–liquid phase equilibrium for the ethanol–acetonitrile system. It can be seen that in the ethanol–acetonitrile system, the azeotrope disappears when AEBA–TEG is added to about 60 wt.%. It is also important to note that ethanol, despite the fact that its boiling point is lower than that of acetonitrile, becomes a hardly volatile component in the presence of AEBA over the entire range of mixture concentrations.

Figure 12 shows the results of modeling the relative volatility of acetonitrile from its solution in ethanol in the presence of AEBA of various molecular structures.

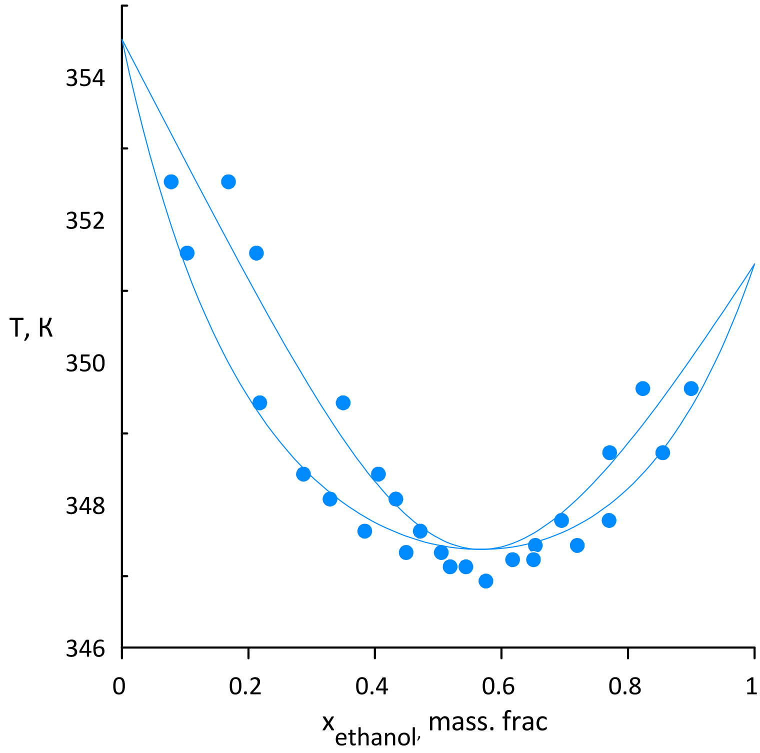

**Figure 11.** TXY diagram for the binary system ethanol–acetonitrile. The line is calculated using the UNIFAC model (Table 2), the dots are the experimental data from [61].

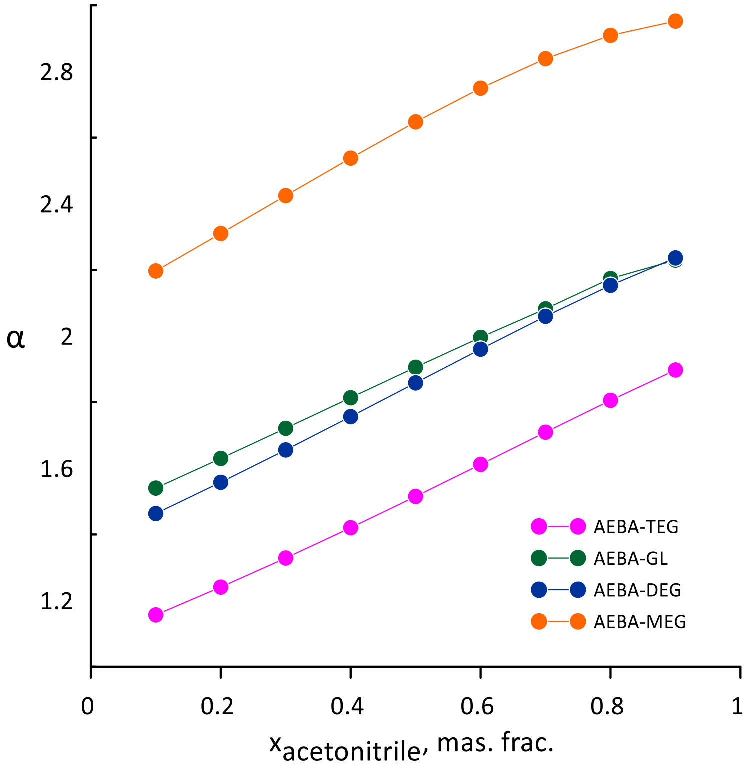

**Figure 12.** Relative volatility of acetonitrile in an azeotropic mixture of ethanol–acetonitrile with the addition of 60 wt.% AEBA-GL/MEG/DEG/TEG.

As for the mixture of acetonitrile–water, an increase in the length of glycol included in AEBA reduces the relative volatility of acetonitrile. At the same time, AEBA-MEG has a high degree of influence on the volatility of acetonitrile.

Thus, the addition of AEBA to binary mixtures of acetonitrile–water and ethanol–acetonitrile makes acetonitrile in these mixtures a highly volatile component. It can be hoped that the addition of AEBA to the ethanol-acetonitrile-water three-component system will make it possible to remove all azeotropes and separate this mixture into components using extractive distillation.

### *3.3. Ethanol-Acetonitrile-Water*

A ternary mixture of ethanol-acetonitrile-water belongs to class 3.1-2 according to Serafimov's classification, which includes 26 classes of admissible topological structures of diagrams according to vapor–liquid equilibrium for ternary mixtures [62,63]. It contains four singular points, three binary azeotropes, and one ternary azeotrope, which divides the diagram into three distillation regions. The triangular line diagram of the residual curves is shown in Figure 13. The calculations were performed on the basis of the UNIFAC model with the parameters from Table 2. The accuracy of the calculated residual curves was verified by comparison with the experimental data presented in Figure 14.

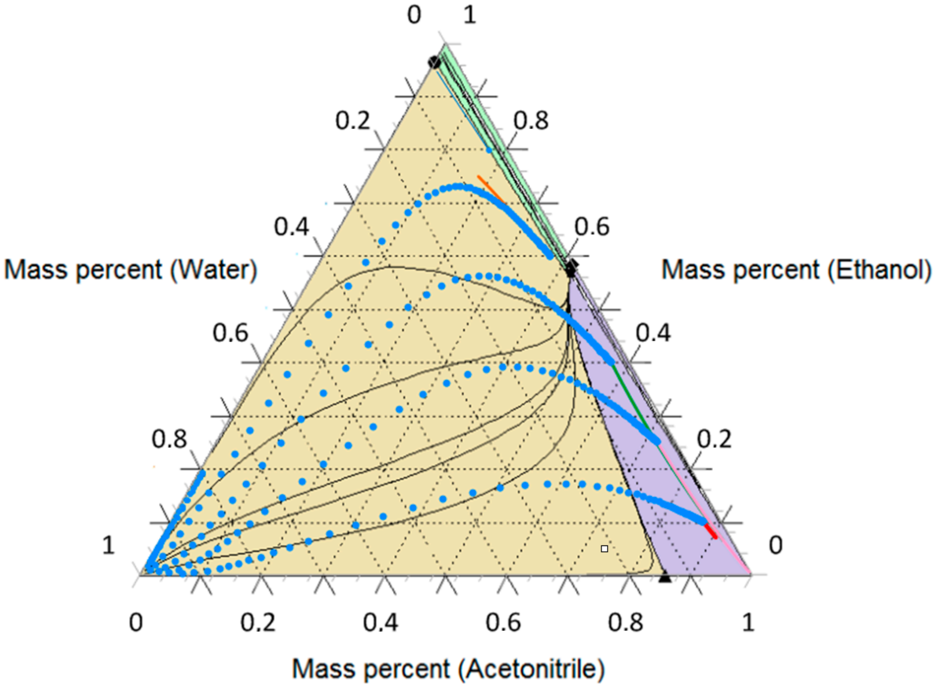

**Figure 13.** Residual curves for a mixture of ethanol-acetonitrile-water. Lines without AEBA–TEG, dots—when 60 wt.% was added to the initial solution of AEBA–TEG.

Figure 13 shows residual curves for a mixture of ethanol-acetonitrile-water with the addition of AEBA–TEG 60 wt.%. As can be seen, the addition of AEBA–TEG to a ternary mixture of ethanol-acetonitrile-water leads to the destruction of three binary azeotropes and a ternary azeotrope, respectively, which indicates the effectiveness of using AEBA–TEG as an entrainer. At the same time, acetonitrile becomes a highly volatile component, water becomes a non-volatile component, and ethanol occupies an average position in terms of volatility.

On the basis of the data obtained, it is possible to propose a conceptual scheme for the separation of a three-component mixture of acetonitrile-ethanol-water by extractive distillation using AEBA–TEG as an extractant. In this scheme, there should be two extractive distillation columns and an extractant regeneration column. In the first column, the distillate will be enriched with acetonitrile, the ethanol-water-AEBA–TEG mixture remains in the bottom, which is fed into the second column. Ethanol is removed in the second column with distillate, and water and AEBA–TEG are accumulated in the bottom. Further, in the regeneration column, water is separated from AEBA–TEG. It should be noted that there are options for carrying out extractive distillation using side sections or partitions in extractive columns, which can reduce the number of columns in the conceptual scheme as well as reduce energy costs. The task of determining the most efficient option for the separation of a three-component mixture of acetonitrile-ethanol-water using extractive distillation requires additional significant research.

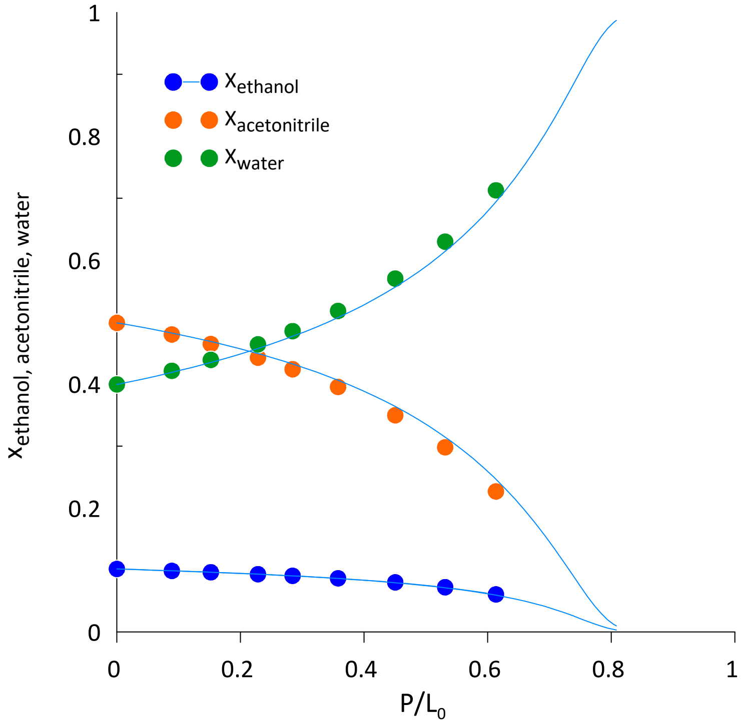

**Figure 14.** Residual curves for a mixture of ethanol-acetonitrile-water, geometric figures—experimental data, line—calculation by the UNIFAC method (Table 2).

## 4. Conclusions

The conducted studies have shown that AEBA is a promising entrainer for the distillation separation of binary and ternary mixtures consisting of acetonitrile, ethanol, and water. The advantages of AEBA include extremely low volatility, the possibility of molecular modification due to the use of various glycols in the synthesis, as well as a high degree of influence on the relative volatility of the components of the mixture under consideration. It was shown that the binary and ternary azeotropes in this system disappear when AEBA–TEG is added to no more than 60 wt.%. To break down some binary azeotropes (acetonitrile–water, ethanol–water [50]), no more than 30 wt.% AEBA–TEG is required.

To simulate the conditions of phase equilibrium of vapor–liquid, according to our own experimental data, previously unknown energy parameters of the UNIFAC model were determined, which describe the interactions of the B, $CH_2N$ groups with the $CH_3CN$ group. Comparison of simulation results with experimental TPXY data and residual curves showed satisfactory agreement. Thus, together with the data from [46], the resulting matrix of UNIFAC parameters (UNIFAC Matrix) Table 2 makes it possible to calculate and predict the activity coefficients of the considered components in a mixture with AEBA of various molecular structures with satisfactory accuracy. The UNIFAC Matrix obtained here Table 2 makes it possible to calculate and predict the activity coefficients of the components under consideration in a mixture with AEBA of various molecular structures with satisfactory accuracy. The average error according to the equilibrium data for the acetonitrile–water mixture was: 3.5% for the concentration of acetonitrile in steam, 0.82% for temperature. For the acetonitrile-water-AEBA–TEG system, the average discrepancy between the experimental and calculated data for the UNIFAC model was 4.5%. For the ethanol–acetonitrile system, the average discrepancy between the experimental and calculated data on the UNIFAC model for the concentration of ethanol in a pair was 3.5%, 0.1% for temperature. This makes it possible to use the UNIFAC model for calculating and searching for optimal schemes for extractive distillation of an ethanol-acetonitrile-water mixture.

**Author Contributions:** I.M.D. designed the study, coordinated the study, carried out data and results analysis, carried out sequence alignments, and drafted the manuscript; A.V.K. conceived of the study, coordinated experimental part of the study, carried out the results analysis, and critically revised the manuscript; A.R.K. carried out separation experiment and collected data; A.V.M. coordinated phase equilibrium experiments, carried out sequences of the study; N.V.M. carried out lab work and participated in the manuscript drafting; All authors have read and agreed to the published version of the manuscript.

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