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RESEARCH ARTICLE

Effect of glucose–citric acid deep eutectic solvent on the vapor–liquid equilibrium of an aqueous ethanol solution

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Abstract

Objectives. To study the effect of a deep eutectic solvent (DES) based on glucose and citric acid on the vapor–liquid equilibrium of an aqueous solution of ethanol.

Methods. A qualitative and quantitative analysis of the conditions of vapor–liquid equilibrium in an ethanol–water–DES ternary mixture was performed based on the open evaporation method and the measurement of *TPxy* data using a Świętosławski ebulliometer. Since the volatility of the DES is negligible in comparison with that of water and ethanol, the composition of the vapor phase was measured by means of Karl Fischer titration. The conditions of vapor–liquid phase equilibrium were modeled using the UNIFAC model.

Results. The open evaporation method was used to determine the curves of residual concentrations for the ethanol–water–DES mixture at various DES concentrations and compositions (glucose–citric acid ratios). *TPxy* data was obtained for the mixture produced by adding 30 wt % DES to an aqueous solution of ethanol at atmospheric pressure. Studies show that DES based on glucose and citric acid has a significant effect on the relative volatility of ethanol in aqueous solution, leading to the disappearance of the azeotropic point. This effect is due to only the presence of glucose. Citric acid does not change the composition of the equilibrium phases, but rather increases the solubility of glucose in aqueous ethanol solutions. This is especially important at high ethanol concentrations, since glucose is poorly soluble in ethanol.

Conclusions. Addition of DES based on glucose and citric acid to an aqueous solution of ethanol leads to the disappearance of the azeotropic point. DES can thus be considered as a promising entrainer for extracting ethanol from aqueous solutions using extractive distillation. Modeling of the conditions of vapor–liquid equilibrium in the ethanol–water–DES system using the UNIFAC model showed a satisfactory level of accuracy. The error in the calculated data increases with increasing the glucose concentration, while remaining acceptable for practical use.

Keywords

vapor–liquid equilibrium, glucose, citric acid, ethanol–water mixture, glucose solubility

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НАУЧНАЯ СТАТЬЯ

Влияние глубоко эвтектического растворителя глюкоза–лимонная кислота на парожидкостное равновесие водного раствора этанола

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Аннотация

Цели. Исследовать влияние глубоко эвтектического растворителя (ГЭР) на основе глюкозы и лимонной кислоты на парожидкостное равновесие водного раствора этанола.

Методы. Для качественного и количественного анализа условий парожидкостного равновесия в трехкомпонентной смеси этанол–вода–ГЭР использовались метод открытого испарения и измерение *TPxy* данных в эбулиометре Свентославского. Так как летучесть ГЭР пренебрежимо мала по сравнению с летучестью воды и этанола, состав паровой фазы измерялся титрованием по методу Карла Фишера. Моделирование условий фазового парожидкостного равновесия проводилось на основе модели UNIFAC.

Результаты. Методом открытого испарения получены линии остаточных концентраций в смеси этанол–вода–ГЭР при разных концентрациях ГЭР и различном составе ГЭР (глюкоза–лимонная кислота). Получены *TPxy* данные при добавлении 30 мас. % ГЭР к водному раствору этанола при атмосферном давлении. Проведенные исследования показали, что ГЭР на основе глюкозы и лимонной кислоты оказывает существенное влияние на относительную летучесть этанола в водном растворе, что приводит к исчезновению азеотропной точки. Это влияние связано только с наличием глюкозы. Лимонная кислота не изменяет состава равновесных фаз, но позволяет увеличить растворимость глюкозы в водных растворах этанола. Это особенно важно при высоких концентрациях этанола, так как глюкоза плохо растворима в этаноле.

Выводы. Добавление ГЭР на основе глюкозы и лимонной кислоты к водному раствору этанола приводит к исчезновению азеотропной точки. Это позволяет рассматривать данный ГЭР в качестве перспективного экстрактивного агента для извлечения этанола из водных растворов с помощью экстрактивной ректификации. Моделирование условий парожидкостного равновесия в системе этанол–вода–ГЭР с использованием модели UNIFAC показали удовлетворительную точность. Ошибка расчетных данных возрастает с увеличением концентрации глюкозы, однако остается приемлемой для практического использования.

Ключевые слова

парожидкостное равновесие, глюкоза, лимонная кислота, этанол-вода, растворимость глюкозы

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INTRODUCTION

Ethanol is an important organic solvent. It is used in many industries: as a reactant in the synthesis of ethers and esters; a solvent in the paint and varnish industry; and as a raw material in the production of household chemicals, medicines, and food products. Ethanol is also one of the most commonly used biofuel components [1–3]. In industrial technologies, ethanol is often present in mixtures with water which are azeotropic. In this regard, the problem arises of separating these mixtures into individual substances.

The separation of azeotropic mixtures is an important requirement in many technological processes. It can be addressed by various methods including: overpressure or vacuum distillation; special distillation methods (azeotropic and extractive distillation)[1] [4];

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[1] Hilmen E.K. *Separation of Azeotropic Ixtures: Tools for Nalysis and Tudies on Batch Distillation Operation*. PhD Thesis. Norwegian Univ. of Science and Technology; 2000. 288 p.

as well as membrane and extraction processes. At the present time, industrial technologies mainly use various distillation methods. For example, in extractive distillation, the mixture to be separated is supplemented with an additional component, or entrainer, which changes the relative volatility of the components of the mixture by interacting with them. The selection of the optimal entrainer from both economic and environmental points of view is an important stage in the development of this technology [5].

Today, four classes of entrainers for separating ethanol–water mixtures exist: organic solvents, solid salts, mixtures of organic solvents with solid salts, and ionic liquids (ILs). Organic solvents used as entrainers may remain in the ethanol obtained, thereby contaminating it. ILs are more environmentally friendly (green) solvents and a promising alternative to conventional organic solvents [6]. The disadvantage of ILs is the complexity of synthesis and separation of the target component with the required purity, thus determining the high cost of the product. Therefore, the search for alternative solvents for the separation of azeotropic mixtures is a challenge. At the present time, research has begun on the use of deep eutectic solvents (DESs) as entrainers. DESs are a new class of environmentally friendly solvents which have many properties similar to ILs [7, 8]. The main advantages of DESs when compared to ILs are the ease of preparation and, as a consequence, their low cost. They also possess the ability to vary the physicochemical properties depending on the nature of the components, their molar ratio, and water content. DESs have virtually zero vapor pressure and are viscous liquids. By increasing the temperature or adding a small amount of water, the viscosity of DESs can be significantly reduced [9–11].

DESs are obtained by mixing two or more components, some of which act as hydrogen bond donors, while others act as hydrogen bond acceptors. The resultant eutectic mixture has a melting point lower than the melting point of pure components [9, 10]. The eutectic point of a mixture is reached at the molar ratio of the mixture components at which the melting point is the lowest[2]. A striking example of a eutectic mixture is the combination of choline chloride and urea. They are solids at room temperature, but when mixed in a certain ratio, they form a liquid solution [12].

In this work, glucose-containing mixtures were studied as DESs for the separation of an ethanol–water mixture.

Glucose, or dextrose (D-glucose), $C_6H_{12}O_6$, is an organic compound. It is a monosaccharide, one of the most common sources of energy in living organisms: a C_6 sugar containing six carbon atoms, an aldehyde group, and five hydroxyl groups [13]. The large number of hydroxyl groups leads to the significant effect of glucose on the relative volatility of the components of an ethanol–water mixture. This gives grounds to consider glucose as an efficient entrainer for the extractive distillation of an ethanol–water mixture. At the same time, glucose under normal conditions is in a solid state and is slightly soluble in ethanol. These circumstances limit the possibility of using glucose as an entrainer. The purpose of this work is to show that the use of the properties of glucose as an entrainer for an ethanol–water azeotropic mixture is possible in its DES with citric acid (CA).

SYNTHESIS OF DES FROM GLUCOSE WITH CA

In order to prepare a DES, glucose monohydrate (*LenReaktiv*, Russia) with a water content of 9.12 wt % was mixed with CA monohydrate (*LenReaktiv*, Russia) with a water content of 8.34 wt % in a round-bottomed flask. This was placed in a thermostated medium of silicone oil (*Solins*, Russia) and continuously rotated. The mixing process was carried out for 2 h until a yellow homogeneous liquid was formed [14]. The temperature of the thermostated medium was maintained at 85–95°C, depending on the ratio of the components. The studies showed that a DES in the liquid phase is formed at various molar ratios of components. In our experiments, the components (glucose and CA) were mixed in the following molar ratio: 0.25 : 0.75; 1 : 1; 0.75 : 0.25; and 0.90 : 0.10. At all ratios, the mixture was in the liquid state. Since the monohydrates were mixed, the water content in the resulting DES was about 9 wt %. An attempt to remove water from the mixture by evaporating it under vacuum resulted in caramelization.

The synthesized DES was stored in glass bottles in a desiccator.

EXPERIMENTAL

In order to assess the effect of the DES mixture on the relative volatility of ethanol in solutions, data on the vapor–liquid phase equilibrium (VLE) in the ethanol–water–DES ternary system is required. The VLE was studied by means of the open evaporation method and the measurement of $TPxy$[3] data using a Świętosławski ebulliometer [15]. In comparison with other methods

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[2] Harris R.C. *Physical Properties of Alcohol Based Deep Eutectic Solvents*. PhD Thesis. University of Leicester; 2009. 188 p.

[3] T is temperature, P is pressure, x is the concentration of the volatile component in the liquid phase, and y is the concentration of the volatile component in the vapor phase.

of measuring equilibrium, the open evaporation method is less labor-intensive and enables the rapid qualitative and quantitative assessment of the effect of adding solvents on the conditions of phase equilibrium in an azeotropic mixture in a certain concentration range [16]. The experimental setup and experimental procedure have previously been described in detail [17–19]. Based on the results of the experiment, the dependence of the composition x of the boiling mixture on its weight L (curve of residual concentration [19]) was calculated according to the following material balance equation:

$$x_i = \frac{\left(L_0 - \sum_{k=1}^{i-1} D_k\right) x_{i-1} + D_i y_i}{L_0 - \sum_{k=1}^{i} D_k} = \frac{\left(1 - \sum_{k=1}^{i-1} e_k\right) x_{i-1} + e_i y_i}{1 - \sum_{k=1}^{i} e_k}, \qquad i = 1 \ldots n, \tag{1}$$

where L_0 and x_0 (at $I = 1$, $x_0 = x_{i-1}$) are the initial weight of the mixture and its initial composition (mass fractions); D_i and D_k are the weights of the ith and kth samples of the distillate, respectively; y_i is the composition of the distillate (mass fractions); n is the number of samples of the distillate; and $e_i = \frac{D_i}{L_0}$ and $e_k = \frac{D_k}{L_0}$ are the relative weights of the ith and kth samples of the distillate, respectively.

Since the volatility of the DES can be neglected, the distillate contains only volatile components. In our case, these are ethanol and water. Therefore, for the convenience of analyzing the results, x and L were taken to be the mass fraction of ethanol in the mixture and the mass of the boiling mixture without taking into the DES into account.

TPxy data in the mixture with DES were measured using a Świętosławski ebulliometer (*Khimlaborpribor*, Russia) [15] (Fig. 1). The temperature was measured with an LT-300-N electronic thermometer (*Termeks*, Russia) with an error of ±0.05°C. The thermometer was installed into pocket *3* filled with electrocorundum. The initial mixture was poured into boiler *1* through condenser *5*. The test mixture was heated with a flexible electric heater wrapped around the outer surface of boiler *1*. The mixture was brought to the boil and maintained for 2.5 h, in order to reach equilibrium of the system. At the same time, samples of the vapor phase were taken, in order to refine the composition of distillate *6*, Samples of the liquid phase were taken, in order to refine the composition of the boiling mixture from the bottom of overflow tube *7*.

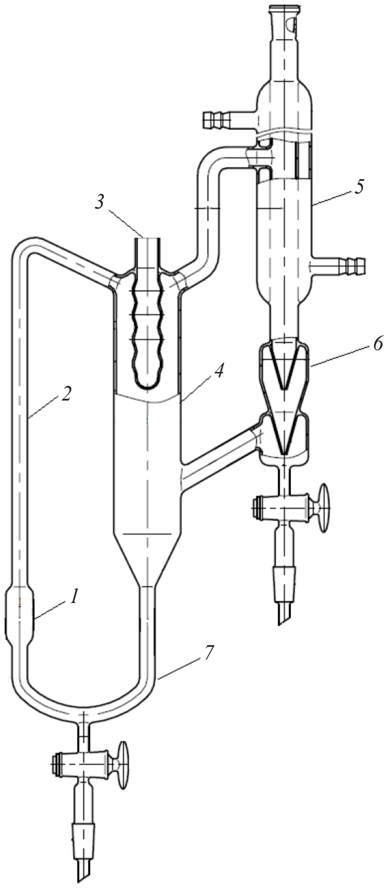

Fig. 1. Świętosławski ebulliometer:
(*1*) boiler,
(*2*) Cottrell pump,
(*3*) thermometer pocket,
(*4*) separation space,
(*5*) condenser,
(*6*) drop counter, and
(*7*) overflow tube [15]

The reliability of the results obtained using this experimental setup was checked by comparing the *TPxy* data on the ethanol–water binary system at an atmospheric pressure of 760 mmHg with experimental results from literature sources in the work [17].

The water content in the initial reagents and in the selected samples of the distillate and the liquid phase from the boiler was determined using a V20 Compact Karl Fischer volumetric titrator (*MettlerToledo*, USA) by means of the Karl Fischer method (with a relative measurement error of ±3%).

MODELING OF THE CONDITIONS OF VAPOR–LIQUID PHASE EQUILIBRIUM

Mathematically, the process of open evaporation of a binary mixture is described by means of the following differential equation:

$$(\bar{e} - 1)\frac{d\bar{x}}{d\bar{e}} = \bar{y}^*(\bar{x}) - \bar{x}, \tag{2}$$

where $\bar{x}$[4] and $\bar{y}^*$ is the liquid composition and its equilibrium vapor composition (mole fractions), respectively; $\bar{e}$ is the mole fraction of the distillate. The VLE condition at moderate pressures has the following form:

$$\bar{y}^* = \frac{P^S(T)\bar{x}\gamma(x,T)}{P}, \tag{3}$$

where P^S and γ are the saturated vapor pressure of the pure component and its activity coefficient in the mixture respectively, while P is the pressure in the system.

By solving Eq. (2) simultaneously with the equilibrium model $\bar{y}^* = f\left(\bar{x}, T, P\right)$, curves of residual concentrations can be calculated. These are experimentally determined using Eq. (1).

The equilibrium distribution of components between the vapor and liquid phases is often characterized by relative volatility:

$$\alpha = \frac{\bar{y}(1-\bar{x})}{\bar{x}(1-\bar{y})}. \tag{4}$$

Given the assumption that α = const, which is acceptable, then if during the open evaporation process, the concentrations in the liquid phase vary within a narrow range, the equilibrium condition (3) takes the following form:

$$\bar{y}^* = \frac{\alpha\bar{x}}{1+(\alpha-1)\bar{x}}. \tag{5}$$

The substitution of condition (5) into Eq. (2) gives the following solution:

$$\bar{e} = 1 - \left[\frac{\bar{x}}{\bar{x}_0}\left(\frac{1-\bar{x}_0}{1-\bar{x}}\right)^{\alpha}\right]^{\frac{1}{\alpha-1}}, \tag{6}$$

where $\bar{x}_0$ is the composition of the initial mixture.

By comparing solution (6) with experimental data on the curves of residual concentrations (1), the relative volatilities of ethanol and water after adding a certain amount of the DES can be determined. Thus, based on the results of the open evaporation method, the effect of the DES on the relative volatility of the components of the mixture being separated can be quantified. For the needs of such a comparison, in solution (6), the molar concentrations need to converted into mass concentrations, taking into account that $\bar{e} = e\frac{M\left(\bar{x}\right)}{M\left(\bar{x}_0\right)}$, where M is the molecular mass of the mixture.

The *TPxy* phase equilibrium conditions in the ethanol–water–DES ternary system were modeled using the UNIFAC model[5] [20]. In this case, the activity coefficients are calculated from the parameters of group components of the molecules of the mixture.

The UNIFAC model divides molecules of substances into group components. The logarithm $\ln\gamma_i$ of the activity coefficient of the *i*th component is the sum of the combinatorial component $\ln\gamma_i^C$ and the residual component $\ln\gamma_i^R$:

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R, \tag{7}$$

which characterize the differences in the sizes of molecules and in the energies on intermolecular interactions, respectively.

In order to determine the combinatorial contribution to the activity coefficient, data needs to entered regarding the parameters of the group volume R and group surface area Q. This data is related to the van der Waals group volume V_k and the surface area A_k of the *k*th functional group [20, 21]:

$$R_k = \frac{V_k}{15.17}, \tag{8}$$

$$Q_k = \frac{A_k}{2.5\cdot 10^9}. \tag{9}$$

The residual (energy) component of the activity coefficient in group models is represented by the sum of group contributions, characterized by the group interaction parameter a_{mn}:

$$\psi_{mn} = \exp\left(\frac{-a_{mn}}{T}\right). \tag{10}$$

The energy group parameter a_{mn} shows the difference in the energies of interactions of groups *n*–*m* and *m*–*n*. Each of the group–group interactions is described by two parameters, a_{mn} and a_{nm}.

The UNIFAC model distinguishes between main groups and subgroups. The subgroups of a main group are energetically identical: i.e., they have the same energy parameters of interaction with other groups

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[4] In this article, a lowercase variable with an overline is mole fraction, a lowercase variable without an overline is mass fraction.

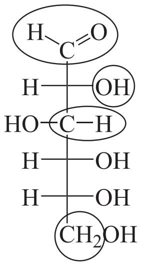
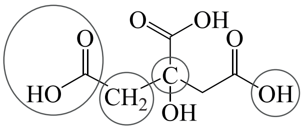
[5] UNIFAC stands for UNIQUAC (**uni**versal **qua**si**c**hemical) Functional-group Activity Coefficients, a semi-empirical system for the prediction of nonelectrolyte activity in nonideal mixtures.

and differ only in geometric characteristics. For example, one main group CH_2 includes subgroups CH_3, CH_2, CH, and C of aliphatic hydrocarbons, and so on.

Forwater molecules and various alcohols, such a partition has already been proposed in the UNIFAC model [20]. The partitions of glucose and CA molecules (Table 1) were taken from the most complete database of group interaction parameters for the UNIFAC model in the form of UNIFAC Matrix 2020, as presented in the Dortmund Data Bank[6]. Thus, glucose consists of the following subgroups: CH_2, 2; C, 1; OH, 1; and COOH, 3. CA consists of the following subgroups: CH_2, 1; CH, 4; OH, 5; and CHO, 1. Table 1 presents the group interaction parameters.

The conformity of the UNIFAC model with the parameters shown in Table 1 was verified by comparing calculated and available experimental data. In the case of an ethanol–water mixture, a satisfactory level of accuracy has previously been shown [17]. With regard to aqueous solutions of glucose and CA, Fig. 2 presents the calculated and experimental [22–24] concentration dependences of boiling points. The average error for the glucose–water mixture was 0.35%, and for the CA–water mixture was 5.2%. This indicates a satisfactory level of accuracy. In addition, Figs. 3 and 4 show the experimental curves of residual concentrations calculated using Eq. (2) for the ethanol–water–DES mixture, the agreement of which is also satisfactory.

Table 1. Group interaction parameters a_{mn}, K

Substance	Formula
D-Glucose	
CA	
Ethanol	
Water	

m n	CH_2	COOH	CHO	OH	H_2O
CH_2	–	315.3	505.7	156.4	300
COOH	663.5	–	497.5	199	−14.09
CHO	677	−165.5	–	−203.6	−116
OH	986.5	−151	529	–	−229.1
H_2O	1318	−66.17	480.8	353.5	–

Note: n and *m* are group interaction parameters.

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[6] https://www.ddbst.com/ddb-search.html. Accessed July 03, 2023.

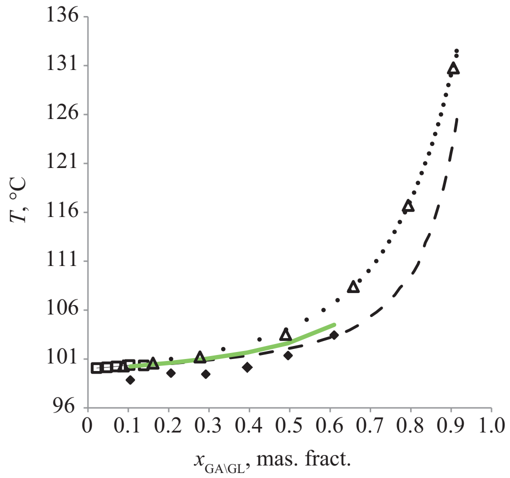


Fig. 2. Boiling points of aqueous solutions of glucose and CA. Glucose–water system ($P = 93.6$ kPa). The solid line represents the results of calculation using the UNIFAC model. The diamonds represent the experimental data [22]. CA–water system ($P = 101.3$ kPa). The dotted line represents the results of calculation using the UNIFAC model. The experimental data is represented by the bullets, squares [23], and triangles [24]

Solubility of DES components in aqueous ethanol solutions

Data on the solubility of glucose in water, ethanol, and their solutions, depending on temperature is available in the literature [25, 26]. The solubility of glucose in water increases linearly with increasing temperature, regardless of ethanol concentration. However, this solubility decreases with increasing ethanol concentration. Thus, the solubility of glucose in water equals 74.1 g glucose/100 g mixture at 60°C, while the solubility of glucose in an 80 wt % aqueous ethanol solution equals 36.2 and 4.2 g glucose/100 g mixture at 60 and 20°C, respectively [25].

Such low solubility of glucose in ethanol does not allow it to be used in its pure form, in order to break up the azeotrope of an ethanol–water mixture.

This work offers an assessment of the changes in the solubility of glucose in an aqueous solution of ethanol in the form of DES in various ratios with CA at 20°C. Solutions at two concentrations of ethanol in water, 80 and 70 wt %, were studied. The solutions were prepared at a given ethanol concentration and various glucoses content by dissolving DES in molar ratios of glucose to CA of 50 : 50, 75 : 25, and 90 : 10. The glucose concentration varied in increments from the solubility concentration of pure glucose to its fivefold value. For example, for the 80 wt % aqueous solution of ethanol, solutions with glucose concentrations of 4, 8, 12, 16, and 20 wt % were prepared. Next, the prepared solutions were heated to 60°C in sealed containers using a magnetic stirrer. The temperature was controlled by a temperature sensor. After complete dissolution, the solutions were cooled to a temperature of 20°C and left for several days. Solubility was determined by the presence or absence of a white crystalline phase in solutions. The studies showed that the use of glucose in the form of DES together with CA enables its solubility to be almost tripled. The effect of the amount of CA was detected only for the 90 : 10 DES (10 mol % CA). In this case, the solubility doubles.

RESULTS AND DISCUSSION

Since the DES consists of two components, one of which (CA) is highly soluble in an ethanol–water mixture, the effect of CA on the VLE of this mixture was studied. The experimental results obtained using the open evaporation method (Fig. 3) and the ebulliometrically measured compositions of the equilibrium phases showed an insignificant effect of CA on the relative volatility of the components of the ethanol–water mixture. Figure 3 demonstrates the curves of residual concentrations after adding 60 wt % CA monohydrate to an aqueous ethanol solution. In its absence they coincide.

The curves of residual concentrations calculated using Eq. (2) and the UNIFAC model also predict an insignificant, although slightly greater in comparison with the experimental data, effect of CA on the volatility of water and ethanol.

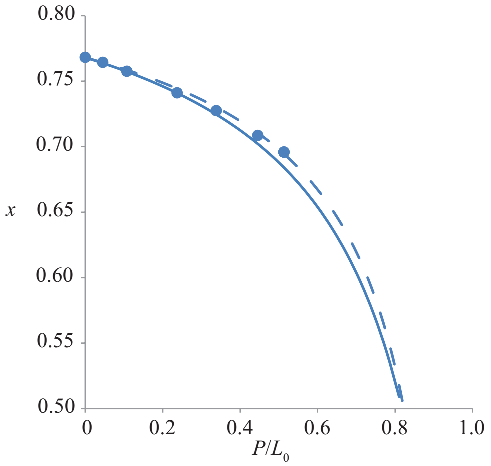


Fig. 3. Curves of residual concentrations of an ethanol–water mixture after adding 60 wt % CA. P is the mass of the ith portion of the distillate P_i; L_0 is the initial mass of the mixture. The points represent experimental data; the solid line, the results of calculation using the UNIFAC model; and the dotted line, the results of calculation without CA

Next, the effect of DES on the relative volatility of ethanol in aqueous solution was studied. Figure 4 illustrates the effect of DES added in an amount of 60 wt % at various glucose and CA contents.

The behavior of the curves of residual concentrations shows that the addition of the DES (Fig. 4) increases the relative volatility of ethanol. This leads to its more rapid depletion in the boiler due to the disappearance of the azeotropic point. Increase in the concentration of glucose in the mixture leads to an increase in the relative volatility of ethanol. Table 2 presents the relative volatilities calculated by comparing formulas (6) and (1). In comparison with the ethanol–water binary mixture, the addition of DES almost doubles the volatility.

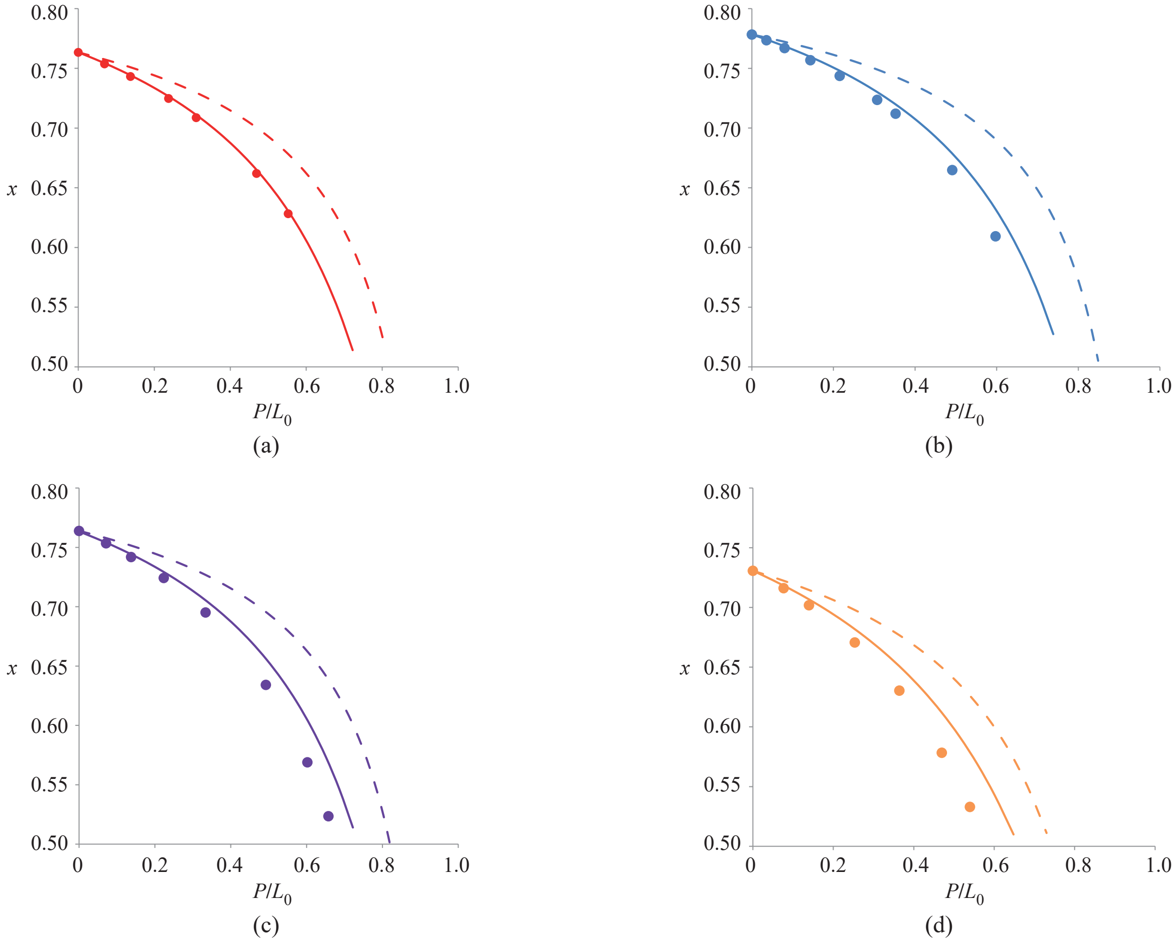
Table 2. Relative volatility of ethanol in an aqueous solution with the addition of DES

Glucose : CA ratio	α
0 : 1	2.0
25 : 75	2.6
50 : 50	2.9
75 : 25	3.0
90 : 10	3.7

Note: α is the relative volatility determined using Eq. (4).

Figure 4 also shows the curves of residual concentrations calculated using Eq. (6) and the UNIFAC model. Discrepancy with the experimental data increases with increased glucose concentration. Since the UNIFAC model satisfactorily describes the VLE in aqueous solutions of glucose (Fig. 4), the discrepancy is most likely due to an error in the description of the energy of interaction of ethanol with glucose.

In this work, *TPxy* data on the ethanol–water system was obtained. The addition of 30 wt % DES in a molar ratio of glucose and CA of 50 : 50 (Figs. 5, 6, and Table 3) leads to the disappearance of the azeotropic point. In this case, the equilibrium compositions of the phases are noticeably affected in the range of ethanol concentrations above 50%. The *TPxy* dependencies calculated using the UNIFAC model showed a satisfactory level of accuracy. Figure 6 also presents the compositions of equilibrium phases after adding 30 wt % CA, coinciding with the data in its absence. This confirms the previously made conclusion about the weak influence of CA on the relative volatility of the components in the ethanol–water mixture.



(a)
(b)
(c)
(d)

Fig. 4. Curves of residual concentrations of an ethanol–water mixture after adding 60 wt % DES at various ratios of glucose and CA, mol %: (a) 25 : 75, (b) 50 : 50, (c) 75 : 25, and (d) 90 : 10. The points represent experimental data; the solid line, the results of calculation using the UNIFAC model; and the dotted line, the results of calculation without the DES

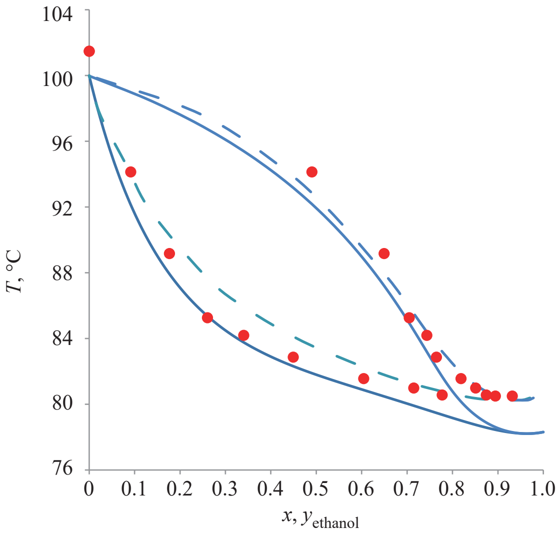


Fig. 5. Phase diagram of the ethanol–water–DES ternary mixture at an atmospheric pressure of 760 mm Hg. The solid line represents the data on the ethanol–water binary mixture; the points, experimental data; and the dotted line, the results of calculation using the UNIFAC model (30 wt % DES)

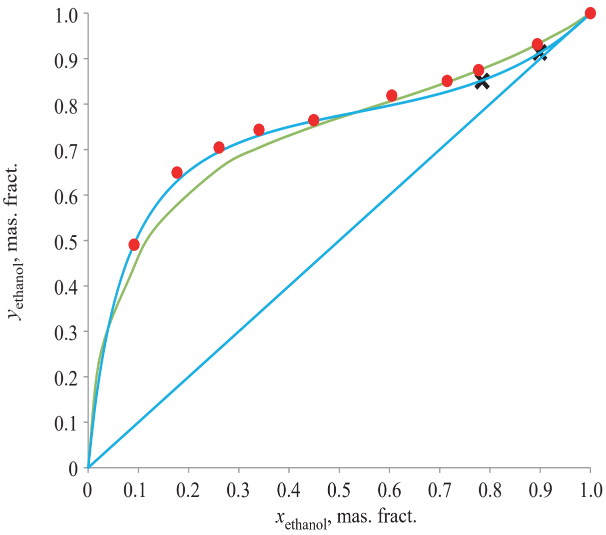


Fig. 6. Liquid–vapor equilibrium in the ethanol–water–DES system at an atmospheric pressure of 760 mm Hg. The blue line represents the data on the binary mixture; the bullets, on the mixture containing 30 wt % DES; and the crosses, on the mixture containing 30 wt % CA. The green line represents the results of calculation using the UNIFAC model

Table 3. Experimental data

T, °C	Mass fraction x_{ethanol}	Mass fraction y_{ethanol}	α	α (without DES)
80.49	0.8945	0.9315	1.60	1.21
80.55	0.7773	0.8746	1.99	1.66
80.98	0.7145	0.8510	2.28	1.91
81.55	0.6043	0.8189	2.96	2.49
82.86	0.4493	0.7645	3.97	3.81
84.19	0.3401	0.7436	5.62	5.11
85.26	0.2604	0.7046	6.77	6.47
89.17	0.1767	0.6493	8.62	8.54
94.13	0.0913	0.4905	9.57	10.99

Note: x_{ethanol} and y_{ethanol} are the ethanol concentrations in the liquid and vapor phases, respectively.

CONCLUSIONS

The studies showed that DES based on glucose and CA has a significant effect on the relative volatility of ethanol in an aqueous solution. This effect is due to only the presence of glucose. CA does not change the composition of equilibrium phases but increases the solubility of glucose in aqueous ethanol solutions. This is especially important at high ethanol concentrations, since glucose is poorly soluble in ethanol. In order to assess the effect of the amount of CA on glucose solubility, the composition of the DES varied from 25 to 90 mol % glucose. However, no such dependence was detected in this concentration range. In most probability, this is not strong.

The *TPxy* data obtained after adding 30 wt % DES to an aqueous solution of ethanol showed the disappearance of the azeotropic point. This allows us to consider DES based on glucose and CA as a promising entrainer for extracting ethanol from aqueous solutions from both environmental and economic points of view. Modeling of the experimental data on VLE using the UNIFAC model showed a satisfactory level of agreement. The error in the calculated data increases with increasing glucose concentration while remaining acceptable for practical use.

Authors' contributions

A.V. Klinov – guidance and scientific advice, analysis of research materials.

A.R. Khairullina – conducting research, analysis of research materials.

The authors declare no conflicts of interest.

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