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Validation for Adequacy Description of the Vapor-Liquid Phase Equilibrium at the Theoretical Step When Separating a Mixture of Light and Heavy Water by Rectification

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Abstract

Validation for adequacy description of the vapor-liquid phase equilibrium at the theoretical step of separation (TSS) was carried out in three stages. At the first stage, the calculated and known experimental data on the $P^o_{H_2O}$ and $P^o_{D_2O}$ vapor pressure of pure component and vapor pressure differences of pure components $\Delta p = pH_2O - pD_2O$ of the H_2O and D_2O components were compared. At the second stage, a comparison of the calculated and known experimental data on the separation coefficient α was considered. The relative deviation of the calculated values from the experimental values did not exceed 0.13%. At the third stage, the calculation of the phase equilibrium at the TSS was performed according to the algorithm developed by the authors, which included the calculation of the activity coefficients of the H_2O and D_2O components for a non-ideal mixture of H_2O-D_2O. The relative deviation of the calculated boiling point of the pure H_2O and D_2O components at a given pressure from the experimental one does not exceed 0.02% for H_2O and 0.5% for D_2O. The analysis of the obtained results indicates an adequate description of the vapor-liquid phase equilibrium at the TSS for the H_2O-D_2O mixture.

Keywords: phase equilibrium; light water; heavy water; activity coefficient

1. Introduction

Water separation into heavy deuterium (D_2O) and light protium (H_2O) is carried out in various countries of the world. Water with a low content of deuterium compared to its content in the standard is considered light water. The Vienna Standard Mean Ocean Water VSMOW-2 is adopted as the main standard which assumes the water quality in the worldwide ocean to be 155.76 ppm D_2O. The main provisions of the standard are set out in [1]. Tap water contains less D_2O compared to the standard. In Moscow tap water, the D_2O content is 145 ppm [2]. Light and heavy water have different properties [3], which are explained by different molecular weights in g/mol equal to 20.02942 (D_2O) and 18.016 (H_2O). Regular intake of light water leads to a decrease in the content of heavy water in the blood plasma that improves the functioning of all body systems [4].

One of the promising ways to separate the H_2O-D_2O mixture components is the vacuum rectification of water. Low-temperature rectification of water at reduced pressure is carried out in rectification columns of the poppet and(or) packing type [5], forming a cascade of columns with direct and recycled product flows. The total number of theoretical separation steps (NTSS) in the columns is quite large, which is due to the small difference in the boiling points of light and heavy water. The calculation of the H_2O and D_2O concentration profiles along the column height in the vapor and liquid phases is a complex task associated

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with the calculation of the equilibrium at the theoretical separation stage.

2. Related work

The simulation of the separation of the homogeneous mixture by the rectification method is based on the accuracy of the description of the vapor-liquid phase equilibrium. The equilibrium compositions of the phases and the boiling point depend on the pressure and composition of the initial mixture. The calculation of the phase equilibrium in real vapor-liquid mixtures is associated with the determination of the activity coefficients of the components γ_i (i is the component number), which depend on the temperature, pressure, and composition of the mixture. Various empirical equations or thermodynamically validated models are used to determine γ_i.

The authors [6] proposed a mathematical model of a packing column for the removal of D_2O from a three-component mixture of H_2O, D_2O, and DHO. It is assumed that a three-component mixture of H_2O, D_2O, and DHO is ideal in both the liquid and vapor phases. The relative volatility coefficients of the components are defined as the ratio of the components' saturation pressures to the saturation pressure of D_2O. Note that in the case of an ideal mixture, the activity coefficients of the components H_2O and D_2O are equal to unity.

In [7], the authors of the present work have derived equations (1) and (2) for the calculation of activity coefficients of light γ_{H_2O} and heavy water γ_{D_2O} under the assumption that the mixture of light and heavy water consisted of just two components H_2O and D_2O:

$$\gamma_{H_2O} = \frac{1}{\dfrac{P_{H_2O}^o}{P}x_{H_2O} + \alpha \dfrac{P_{D_2O}^o}{P}x_{D_2O}}, \qquad (1)$$

$$\gamma_{D_2O} = \frac{1}{\dfrac{1}{\alpha}\dfrac{P_{H_2O}^o}{P}x_{H_2O} + \dfrac{P_{D_2O}^o}{P}x_{D_2O}}, \qquad (2)$$

where $P_{H_2O}^o$ and $P_{D_2O}^o$ are the vapor pressures of pure components H_2O and D_2O at a given temperature and external pressure P; α is the separation coefficient; x_{H_2O} and x_{D_2O} are molar fractions of H_2O and D_2O components.

It is shown that the H_2O-D_2O mixture is not ideal, and the concepts of relative volatility coefficient and separation coefficient for the H_2O-D_2O mixture are not identical. The proposed algorithm for calculating the rectification column for separating a mixture of light and heavy water consists of a column calculation module, which includes a module for calculating the equilibrium at the TSS and a module for calculating the boiling point at the TSS. According to the developed algorithm, the authors conducted a calculation of the packing column installed last in the cascade of five rectification columns intended for deprotization of the heavy-water moderator. The obtained calculated data on the separation of this mixture are in good qualitative and quantitative consistency with the experimental data [5].

In this article, the adequacy of the description of the vapor-liquid phase equilibrium in the separation of a mixture of light and heavy water by rectification is verified by comparing the known experimental and calculated data of the boiling points of the H_2O and D_2O components when changing the concentration of D_2O in the liquid phase from 0 to 100% at pressures ranging from 20 to 101.325 kPa (atmospheric pressure). The separation coefficients are calculated depending on the pressure and temperature of the mixture.

3. Methods

The calculations were performed according to the software developed by the authors in the Borland Pascal language using numerical analysis methods according to the algorithm described in [7] in the form of flow diagrams for calculating the rectification column, phase equilibrium at the TSS, and calculating the boiling point at the TSS.

4. Results and discussion

The verification of the description adequacy of the phase equilibrium at the TSS is conducted in three stages.

At the first stage, the accuracy of the description of the vapor pressures of pure components $P_{H_2O}^o$ and $P_{D_2O}^o$ is checked using the known Antoine equation, whose mathematical notation and the Antoine constants for the H_2O and D_2O components are given in [7].

Table 1 shows the experimental [8-10] and calculated data of the vapor pressures of pure components $P_{H_2O}^o$ and $P_{D_2O}^o$ of H_2O and D_2O,

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calculated by the Antoine equation. The analysis of the obtained results shows the high accuracy of the empirical equation and the Antoine constants for the H_2O and D_2O component.

Table 1. Experimental and Calculated Data of Vapor Pressures of H_2O and D_2O Components

Temperature, °C	Experimental data and Source						Data, calculated by Antoine equation			
	[8]		[9]		[10]					
	Vapor pressures of pure component									
	$P^o_{H_2O}$	$P^o_{D_2O}$	$P^o_{H_2O}$	$P^o_{D_2O}$	$P^o_{H_2O}$	$P^o_{D_2O}$	$P^o_{H_2O}$	$P^o_{D_2O}$	$P^o_{H_2O}$	$P^o_{D_2O}$
	kPa				mm Hg		kPa		mm Hg	
20	2.337	2.011	2.3388	2.0	17.5	16.2	2.339	2.009	17.54	15.07
30	4.242	3.731	4.2455	3.7	31.8	27.9	4.247	3.714	31.85	27.86
40	7.375	6.598	7.3814	6.5	55.3	49.2	7.385	6.5622	55.39	49.22
50	12.335	11.198	12.344	11.1	95.5	83.4	12.350	11.1327	92.63	83.50
60	19.919	18.305	19.932	18.2	149.2	136.1	19.940	18.2055	149.56	136.55
70	31.161	28.940	31.176	28.8	233.5	215.5	31.185	28.799	233.91	216.01
80	47.359	44.400	47.373	44.2	355.1	331.2	47.384	44.207	355.41	331.58
90	70.108	66.270	70.117	66.1	525.8	495.1	70.127	66.025	526.00	495.23
100	101.325	96.460	101.32	96.2	760	721.6	101.332	96.186	760.05	721.45
101.43	107.322	102.297	107.315	-	-	-	106.612	101.310	799.66	759.89
110	143.260	137.280	143.24	-	-	-	143.252	136.974	1074.48	1027.39

Fig. 1 shows a comparison of the experimental data on the pressure difference of pure components ($\Delta p = pH_2O – pD_2O$), kPa, given in [11], and the calculated data.
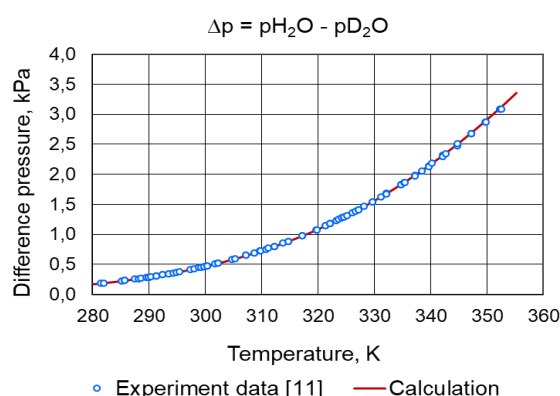

Fig. 1. Comparison of Experimental and Calculated Data on the Vapor Pressures Difference of Pure Components ($\Delta p = pH_2O – pD_2O$) between the H_2O и D_2O

The analysis of Fig. 1 and Table 1 shows the applicability of the Antoine equation for the calculation of vapor pressures of pure H_2O and D_2O components with high accuracy.

At the second stage, the experimental data on the separation coefficients are compared with conducted calculations. Since in addition to the D_2O and H_2O molecules, natural water contains also HDO molecules, based on the assumption that the vapor pressure of HDO is the average geometric value of the vapor pressures of D_2O and H_2O, and the equilibrium constant of the reaction $H_2O + D_2O \rightleftarrows 2HDO$ in the vapor phase is equal to 4, Urey obtained an expression according to which the separation coefficient α is equal to the square root of the ratio of the vapor pressures of the pure H_2O to D_2O components [12]

$$\alpha = \sqrt{\frac{P^o_{H_2O}}{P^o_{D_2O}}} \qquad (3)$$

Fig. 2 shows the experimental data of the separation coefficient α [13, 14] and the curve calculated according to equation (3), in which the vapor pressures of pure components $P^o_{H_2O}$ и $P^o_{D_2O}$ of the H_2O and D_2O is calculated by the Antoine equation. The relative deviation of the calculated value of the separation coefficient from the experimental one does not exceed 0.13%.
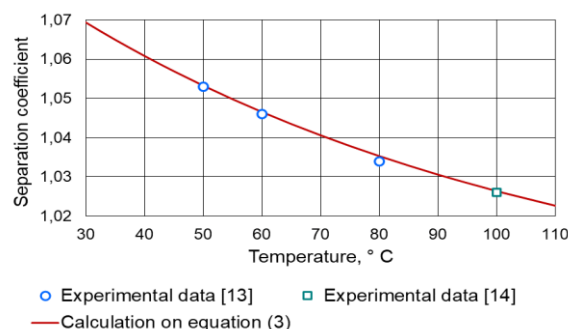

Fig. 2. Experimental and Calculated Data of the Separation Coefficient for the H_2O-D_2O Mixture

At the third stage, calculations were carried out to determine the phase equilibrium at the TSS, described in [7], in which the equations of Antoine and Urey were used.

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Fig. 3 shows the experimental data [9] and the calculated curves illustrating the dependence of the boiling point of the pure H_2O and D_2O components on the pressure. The computational procedure includes the calculation of the phase equilibrium at the TSS, at which the activity coefficient of light water γ_{H_2O} and heavy water γ_{D_2O}, like that for the pure component, is assumed to be unity.
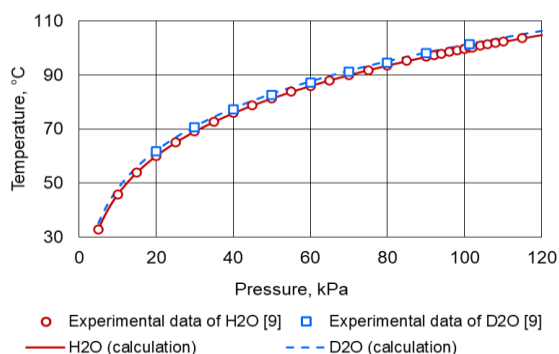

Fig. 3. Dependence of the boiling point of the Pure H_2O and D_2O Components on Pressure

Based on the calculation of the phase equilibrium at the TSS, the boiling points of the H_2O-D_2O mixture were determined depending on the D_2O concentration in the liquid phase ranged from 0 to 100% for pressures from 20 to 101.325 kPa (atmospheric). In Fig. 4, lines show the calculated data of the change in the boiling point of the H_2O-D_2O mixture as a function of the pressure and the content of D_2O in the mixture. The activity coefficients of light water γ_{H_2O} and heavy water γ_{D_2O} are calculated using equations (1) and (2). The relative deviation of the calculated boiling point of the pure component from the corresponding experimental value does not exceed 0.02% for H_2O and 0.5% for D_2O.

The analysis of the obtained results indicates an adequate description of the vapor-liquid phase equilibrium at the TSS for the H_2O-D_2O mixture.
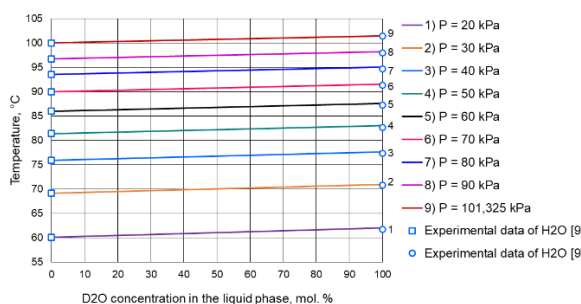

Fig. 4. Boiling Point of the H_2O-D_2O Mixture Depending on the Concentration of D_2O in the Liquid Phase at Different Pressures

5. Conclusion

The simulation of the rectification process in the rectification column is based on the calculation of the vapor-liquid phase equilibrium at the TSS. The accuracy of the description of the phase equilibrium influences the quality of the separated products and NTSS. When separating water into light and heavy water, the NTSS is quite big, and therefore the separation occurs in a cascade of several columns, rather than in a single column. In this article, the calculations, carried out taking into account the phase equilibrium at the TSS, have shown a high convergence of the calculated and experimental data, accumulated in the literature. The method of calculating the rectification column for separating the mixture into light and heavy water, including the calculation of the phase equilibrium at the TSS, can be used to simulate a cascade of tray-type rectification columns equipped with direct and recycle flows, in order to optimize the technological scheme, increase product yield, and reduce capital and energy costs of the separation process.

6. Conflicts of interest
There are no conflicts to declare.

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