PECULIARITIES OF DIETHYLAMINE DISTILLATION PROCESS FROM CALCIUM CHLORIDE AQUEOUS SOLUTION

Volodymyr PANASENKO, Candidate of Technical Sciences, Senior Teacher
Vinnytsia National Agrarian University
Dmytro DEINEKA, Candidate of Technical Sciences, Associate Professor
National Technical University "Kharkiv Polytechnic Institute"

ПАНАСЕНКО Володимир Володимирович, к.т.н., старший викладач
Вінницький національний аграрний університет
ДЕЙНЕКА Дмитро Миколайович, к.т.н., доцент
Національний технічний університет «Харківський політехнічний інститут»

The research investigates the distillation process of diethylamine $((C_2H_5)_2NH)$ from aqueous solutions of calcium chloride, which is crucial in the potassium carbonate production process. Despite the significance of phase equilibria for the system $CaCl_2 – (C_2H_5)_2NH – H_2O$ in optimizing distillation processes, the literature lacks comprehensive data, particularly at low pressures. This study aims to bridge that gap by examining the distillation kinetics at pressures of 47.996, 21.331, and 7.999 kPa. Experimental results show that when the calcium chloride content exceeds 27–28% by mass, the solution temperature increases, marking the transition from distillation to more energy-intensive processes due to the formation of hydrates like $CaCl_2·12H_2O$. The findings highlight that reducing pressure to 7.999 kPa nearly doubles the distillation rate compared to pressures above 21.331 kPa. A general kinetic model was developed, describing the relationship between evaporated water, diethylamine concentration, process time, and pressure. This model, derived from first-order kinetics, allows for accurate predictions of diethylamine content over time without directly accounting for pressure variations. Additionally, the research emphasizes that water evaporation kinetics are closely tied to the diethylamine content, as water evaporation accelerates significantly once the amine concentration drops below a certain threshold. These insights contribute to the development of efficient distillation strategies, minimizing reagent loss, and optimizing steam consumption. The derived equations and models are applicable not only for laboratory experiments but also for scaling up to industrial processes, offering practical tools for technological calculations and improving the sustainability of potassium carbonate production.
Key words: mineral fertilizers, potassium carbonate, distillation, solution, diethylamine, calcium chloride.
*Eq. 6. Fig. 8. Table. 1. Ref. 12.*

1. Problem formulation

The process of distillation of $(C_2H_5)_2NH$ is an integral part of the potassium carbonate production technology. However, data on phase equilibria for the system $CaCl_2(sol) – (C_2H_5)_2NH(sol) – H_2O$ are limited in the literature, and for low pressures, they are completely absent. While such information is not only of theoretical interest, as this system is a subject for studying the regularities of the distillation process, it also has practical significance, which is necessary for determining the optimal distillation parameters, developing a technological scheme for the regeneration process of $(C_2H_5)_2NH$, and largely determining the irreversible losses of the costly reagent and the consumption of steam. The literature provides suggestions for the regeneration of amines from their chlorides, using calcium hydroxide as one of the cheapest and most effective reagents for this purpose [1–6]. For this, it is necessary to understand the direction of the reaction.

$$Ca(OH)_{2(sol)} + 2(C_2H_5)_2NH_2Cl_{(sol)} = CaCl_{2(sol)} + 2(C_2H_5)_2NH_{(sol)} + 2H_2O_{(liq)} \qquad (1)$$
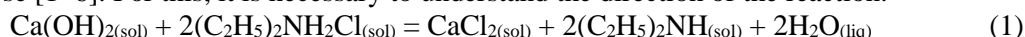
and the possibility of the most complete distillation of $(C_2H_5)_2NH$ for its return to the technological cycle, similar to how it occurs in the closed cycle of ammonia use in soda ash production. According to thermodynamic data [7], reaction (1) is reversible and proceeds at a noticeable rate even at standard temperature 298.15 K and pressure 101.32 kPa. Based on the research of the authors [8, 9], pressure plays an important role in the distillation process. Thus, when the pressure decreases from 101.32 to 48.64 kPa, an
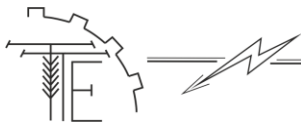
increase in the calcium chloride content in the liquid phase leads to an increase in the concentration of $(C_2H_5)_2NH$ in the vapor at the same temperatures.

2. Analysis of recent research and publications

Recent studies have explored the distillation of diethylamine from aqueous calcium chloride solutions, focusing on phase equilibria and distillation kinetics. Research on the diethylamine-water system indicates the absence of azeotropic behavior, facilitating separation processes [1].

Additionally, investigations into solid–liquid equilibria involving diethylamine and ionic liquids provide insights into phase behavior relevant to distillation [2, 3].

A method for recovering diethylamine from filtrate liquids in industrial processes has been patented, highlighting its practical significance [4, 5].

Furthermore, studies on the solubility and phase equilibria of related systems, such as $CaCl_2$-$SrCl_2$-$BaCl_2$-H_2O, offer valuable data for understanding complex aqueous solutions [6, 7].

These findings contribute to optimizing distillation strategies and enhancing the efficiency of processes involving diethylamine and calcium chloride solutions [8].

The distillation process of $(C_2H_5)_2NH$ from the initial aqueous solution containing 20% by mass of $CaCl_2$ and 5% of $(C_2H_5)_2NH$ was carried out by the method of single-stage evaporation [9, 10]. In the collected sample, the content of $(C_2H_5)_2NH$ was determined using the Kjeldahl distillation method, calcium ion content was established by the complexometric titration method, and the chloride ion content was determined argentometrically using the automatic titration block BAT-15. Experimental data were processed using mathematical statistics and regression analysis methods [11, 12] with the help of an applied software package.

3. The purpose of the article

The aim of this study is to investigate the distillation process of diethylamine $((C_2H_5)_2NH)$ from aqueous calcium chloride $(CaCl_2)$ solutions under low-pressure conditions to determine the phase equilibrium patterns in the $CaCl_2 – (C_2H_5)_2NH – H_2O$ system. The research focuses on evaluating the influence of $CaCl_2$ concentration on the diethylamine content in the vapor phase

4. Results and discussion

The initial data for analysis were taken from experimental measurements: time from the start of the experiment, minutes; pressure over the solution, kPa; solution temperature, ºC; and the content of $CaCl_2$ and, accordingly, $(C_2H_5)_2NH$, %.

As seen from the table and Figure 1, when the calcium chloride content in the solution exceeds 27-28%, the solution temperature begins to slowly increase. Based on the dependencies for all three different pressure values, it can be assumed that the solution temperature does not rise until the calcium chloride content exceeds a certain value, which indicates the physical process of distillation up to this concentration. It should be noted that in all cases, the molecular ratio between water and anhydrous calcium chloride, at which the temperature increase begins to be observed, is 15:1.

Table 1.

Results of kinetic studies of diethylamine distillation from aqueous calcium chloride solution

| Time, min	Pressure over the solution, kPa								
	47,996			21,331			7,999		
	Solution temperature, ºC	Mass fraction of the component, %		Solution temperature, ºC	Mass fraction of the component, %		Solution temperature, ºC	Mass fraction of the component, %	
		$(C_2H_5)_2$ NH	$CaCl_2$		$(C_2H_5)_2$ NH	$CaCl_2$		$(C_2H_5)_2$ NH	$CaCl_2$
5	83,0	0,750	20,96	64,0	1,290	20,83	44,0	0,889	20,88
10	86,0	0,145	21,37	67,0	0,515	21,38	48,0	0,708	21,72
15	86,5	0,107	23,45	67,5	0,126	22,90	50,0	0,202	23,90
20	87,5	0,087	23,80	70,0	0,074	24,60	50,5	0,190	27,06
30	88,0	0,077	25,73	71,0	0,069	26,25	52,0	0,093	29,29
40	89,0	0,041	28,08	72,0	0,059	30,55	56,0	0,087	30,40
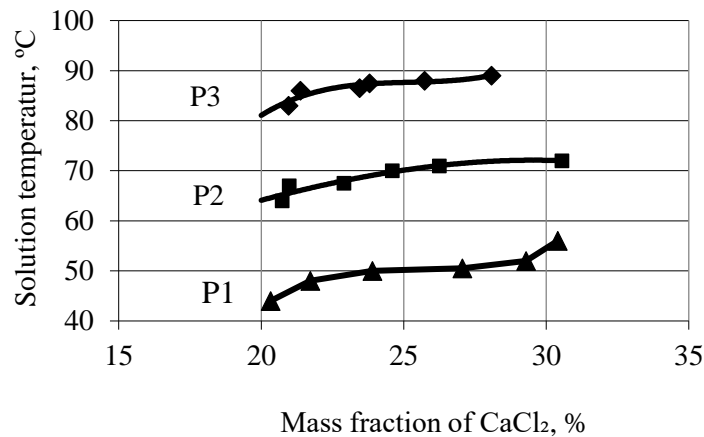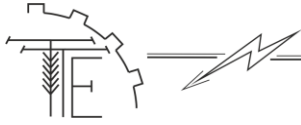
**Fig. 1 – Dependencies of solution temperature on calcium chloride content
Designations: P_1 – 47.996 kPa; P_2 – 21.331 kPa; P_3 – 7.999 kPa.**

It can be assumed that with a molecular ratio of H_2O to $(C_2H_5)_2NH$ of approximately (12-15):1, water is in a bound state, forming something like a liquid crystalline hydrate $CaCl_2 \cdot 12H_2O$, the destruction of which requires significant energy and, consequently, higher temperatures. A lower temperature corresponds to a higher concentration of $(C_2H_5)_2NH$.

The dependence of the solution temperature on the calcium chloride content is nonlinear with respect to pressure and can be described with an accuracy of 1–2°C for the horizontal temperature section (Fig. 2) as a logarithmic function: $t_p = 20.59 \cdot \ln(P) + 0.034$, where t_p is the solution temperature, °C; P is the pressure, kPa. The coefficient of determination is $R^2 = 0.995$.
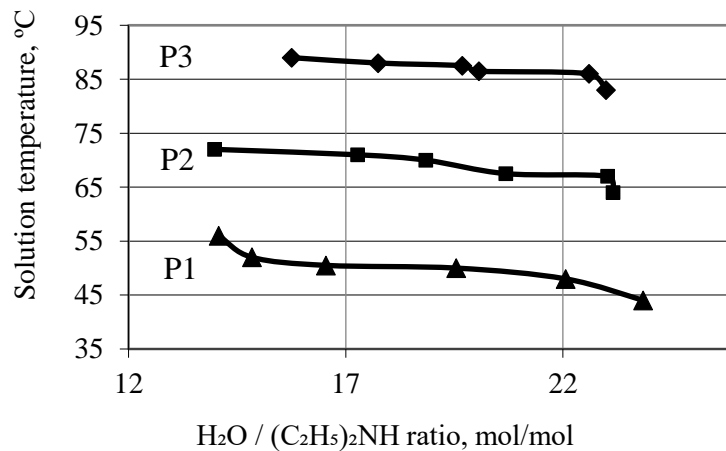

Fig. 2. Dependencies of solution temperature on the molecular ratio between H_2O and $(C_2H_5)_2NH$

Since this system is a three-component one, to describe it, it is sufficient to know the patterns of change for two components. At the same time, the mass of calcium chloride in the system does not change (it remains in the solution). The calcium chloride content in the solution cannot be considered a kinetic indicator, as it is secondary, although it should be taken into account as a possible influencing parameter.

Thus, the kinetics of the process can be represented by the kinetics of the changes in the amounts of H_2O and $(C_2H_5)_2NH$. The main indicator for $(C_2H_5)_2NH$ can be its content in the solution (C_{DEA}). For water, the main indicator can be the amount of evaporated water.

As seen from the kinetic dependencies for H_2O and $(C_2H_5)_2NH$ (Fig. 3), there is a clear mutual relationship between them. Until the content of $(C_2H_5)_2NH$ in the solution decreases below a certain value, the water evaporation process is essentially blocked. The evaporation rate at the initial stage (up to 15 minutes) practically does not depend on pressure. At the same time, a decrease in pressure significantly increases the rate of water evaporation at low concentrations of $(C_2H_5)_2NH$ in the solution.
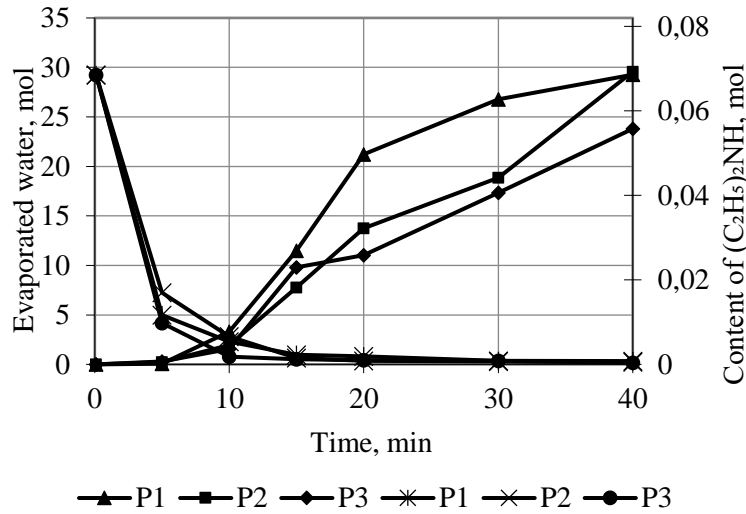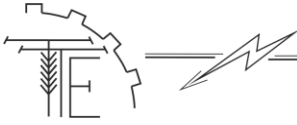
Fig. 3. Kinetic dependencies for evaporated water and (C₂H₅)₂NH content in the solution

For technological calculations, the content of $(C_2H_5)_2NH$ over the distillation time (Fig. 4) can be calculated without considering the influence of pressure using an equation corresponding to first-order kinetics:

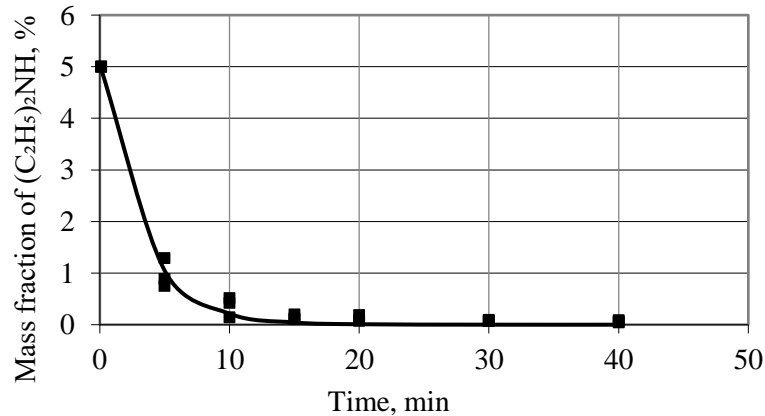$$C_{DEA} = 5{,}12 \cdot e^{-\tau/3,15} \qquad (2)$$

Fig. 4. Dependence of (C₂H₅)₂NH content in the solution on distillation time However.

A more detailed study of the data reveals differences between kinetic dependencies for different pressures, which is particularly evident when using not the content of $(C_2H_5)_2NH$ but its logarithm (Figure 5).
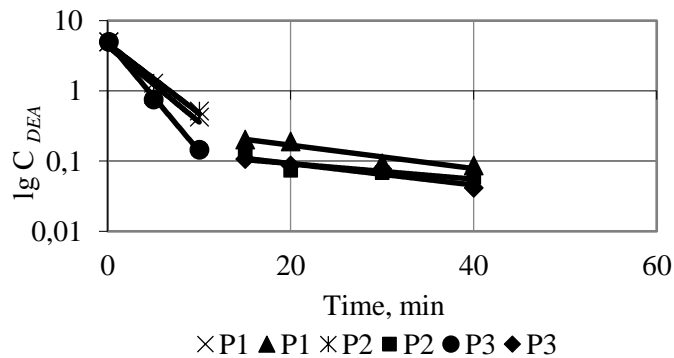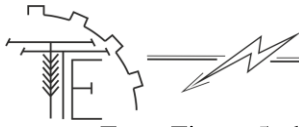

Fig. 5. Kinetic dependence of (C₂H₅)₂NH content in the solution on distillation time in logarithmic coordinates

From Figure 5, the division of kinetic dependencies into two sections – high and low distillation rates – is clearly visible. For the first section (up to 15 minutes), the kinetics follow the previously provided dependence (3). For the second section, the coefficients have different values:

$$C_{DEA} = 0,17 \cdot e^{-\tau/31,2}, \text{ P1} = 47,996 \, \& \, \text{P2} = 21,331 \text{ kPa} \tag{3}$$

$$C_{DEA} = 0,17 \cdot e^{-\tau/31,2}, \text{ P3} = 7,999 \text{ kPa} \tag{4}$$

The differences in the coefficients for lower pressures are statistically significant and indicate an almost twofold increase in the distillation rate when the pressure is reduced to 7.999 kPa compared to pressures above 21.331 kPa. For technological calculations, a more convenient general dependence for any pressure (P) would be one that accurately describes all observed values for the logarithm of $(C_2H_5)_2NH$ content (lgC_{DEA}) and is continuous (Fig. 6).

$$C_{DEA} = \left(C_{DEA}^0 - C_{DEA}^{min}\right) \cdot e^{-\frac{\tau}{\tau_1}} + C_{DEA}^{min} \cdot e^{-\frac{\tau}{\tau_1}}, \, C_{DEA}^0 = 5\% \, mass$$

$$C_{DEA}^{min} = 0,125 - \left(\frac{2,39}{P}\right)^2; \, \tau_1 = 3,505 - \left(\frac{P}{44,47}\right)^2; \, \tau_2 = 42,5.$$
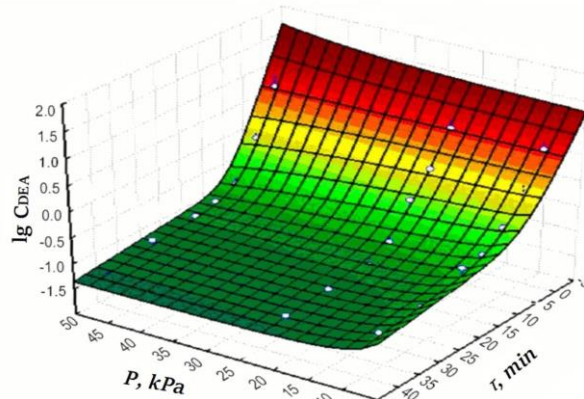

Fig. 6. Kinetic dependencies of $(C_2H_5)_2NH$ content in the solution on distillation time and pressure

Considering that the value is much smaller than the initial content of $(C_2H_5)_2NH$ in the solution, the general equation can be simplified without significant error to the following form

$$C_{DEA} = C_{DEA}^0 \cdot e^{-\frac{\tau}{\tau_1}} + C_{DEA}^{min} \cdot e^{-\frac{\tau}{\tau_1}} \tag{5}$$

The coefficient of determination is $R^2 = 0.986$, and the root mean square error of the concentration logarithm is 0.03. A high coefficient of determination (greater than 0.95) indicates a functional relationship between the variables [11, 12]. The rate of water evaporation, as mentioned earlier, depends on the $(C_2H_5)_2NH$ content in the solution – its decrease at the 15th minute leads to a sharp increase in the water evaporation rate (Fig. 7).
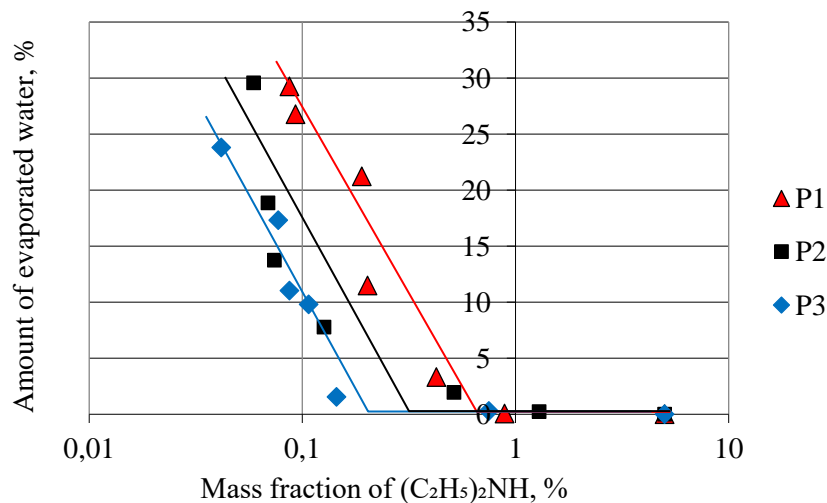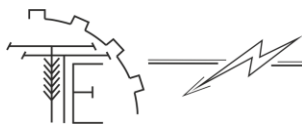

Fig. 7. Dependence of the amount of evaporated water on the $(C_2H_5)_2NH$ content in the solution and distillation pressure

Understanding this pattern allowed for the derivation of a general equation that links the amount of evaporated water (W) over a certain time period with the content of $(C_2H_5)_2NH$ in the solution and the pressure.

$$W = ln \cdot \left[e^{20,45-38,37 \cdot \left(1-e^{\frac{-P}{6,79}}\right) \cdot ln \frac{0,1442+0,8640 \cdot \left(1-e^{\frac{-P}{6,79}}\right)}{c_{DEA}} + 1} \right] \qquad (6)$$

Considering that equation (6) is derived from laboratory experimental data and corresponds to the experimental results within the measurement error, it can be used for technological calculations and describing the distillation process at a larger industrial scale. It should be noted that for water evaporation kinetics, the equation does not include time, which indicates that the amount of evaporated water is fully determined by the evaporation kinetics of $(C_2H_5)_2NH$. Since the content of $(C_2H_5)_2NH$ depends on time, the amount of evaporated water, and consequently the mass fraction of calcium chloride in the solution, can be calculated for any time interval (Fig. 8).
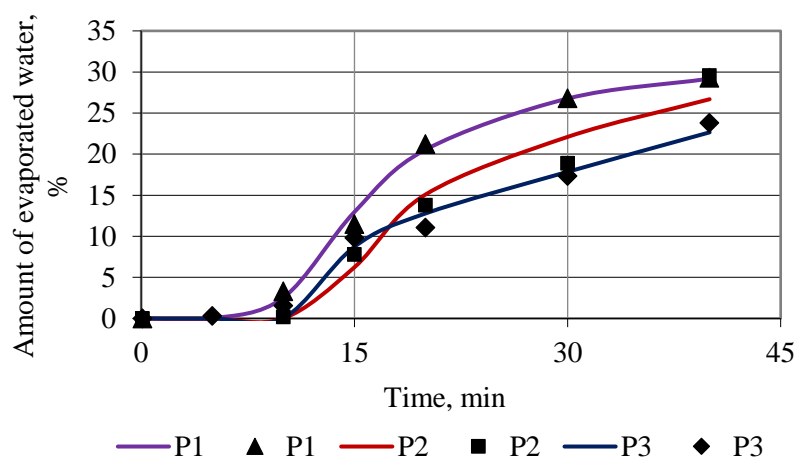

Fig. 8. Dependence of the amount of evaporated water on time and distillation pressure of $(C_2H_5)_2NH$

5. Conclusion

Experimental studies have established that at pressures of 47.996, 21.331, and 7.999 kPa, the temperature of the solution does not increase until the calcium chloride content exceeds a certain value (27 – 28% by mass), indicating the physical process of distillation of $(C_2H_5)_2NH$ at this concentration. It has been shown that the content of $(C_2H_5)_2NH$ in the solution over the distillation time can be calculated without considering the influence of pressure using an equation that corresponds to first-order kinetics. It has been determined that the distillation rate when reducing pressure to 7.999 kPa is nearly double compared to pressures above 21.331 kPa. Based on the identified patterns, a general relationship has been obtained that links the amount of evaporated water over a certain time period with the content of $(C_2H_5)_2NH$ in the solution and the pressure, which can be used for technological calculations and for describing the distillation process at a larger industrial scale.

References

1. Brown, P., & Smith, J. (2015). *Chemical thermodynamics of amines and their derivatives*. Journal of Chemical Thermodynamics, 85, 12–23. https://doi.org/10.1016/j.jct.2015.05.001. [in English].
2. Chavan, A., & Prasad, R. (2014). Calcium chloride hydrates: Structural and thermal analysis. *Journal of Molecular Structure*, 1087, 210–220. https://doi.org/10.1016/j.molstruc.2014.05.023. [in English].
3. Davis, M. J., & Lee, R. T. (2013). Distillation kinetics of binary and ternary systems at reduced pressures. *Industrial & Engineering Chemistry Research*, 52(6), 2457–2463. https://doi.org/10.1021/ie302451p. . [in English].
4. Gupta, K., & Roy, S. (2011). Reclamation of amines from aqueous systems using calcium hydroxide. *Chemical Engineering Journal*, 169(1), 125–133. https://doi.org/10.1016/j.cej.2010.10.056. [in English].
5. Kaye, G., & Laby, T. H. (1999). *Thermodynamic properties of chemical systems*. Cambridge University Press. [in English].
6. Smith, D. W., & Johnson, P. (2016). Regression analysis for chemical process optimization. *Statistical Methods in Chemical Engineering*, 12(2), 45–58. [in English].
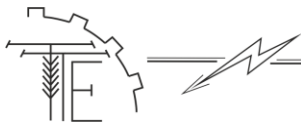
7. Panasenko, V.V., Hryn, G.I., Loboiko, V.A., Lavrenko, A.A., Kobzev, A.V. (2012). Thermodynamics of Chemical Reactions in the Technology of Potassium Carbonate Production. Integrated. *Technologies and Energy Saving, 1,* 28–36. [in Ukrainian].

8. Panasenko, V.O., Mazunin, S.A., Hryn, G.I., Vaisbrod, A.A., Bondarenko, I.V. (1997). Study of the Desorption Process of Diethylamine. *Proceedings of the International Scientific Conference "Information Technologies: Science, Technology, Education, Health".* May 12–14, Kharkiv: KhDPU, 86–89. [in Ukrainian].

9. Panasenko, V.O., Mazunin, S.A., Hryn, G.I. (2000). Liquid-Vapor Equilibrium in the System Water – Diethylamine – Calcium Chloride. *Bulletin of Kharkiv State Polytechnic University, 105*, 76–79. [in Ukrainian].

10. Radchenko S.G. (2005). *Stable Methods for Evaluating Statistical Models: Monograph.* Kyiv: PP "Sansparel". [in Ukrainian].

11. Zhao, Y., & Li, W. (2021). Advanced titration techniques for ion determination in industrial chemical processes. *Analytical Chemistry*, 93(11), 4567–4575. https://doi.org/10.1021/acs.analchem.0c04952. [in English].

12. Kaliuzhnyi, M.I., Kravchuk, S.H. (2018). *Doslidzhennia protsesu reheneratsii aminiv u tekhnolohii zamknutoho tsyklu vyrobnytstva* [Study of the process of regeneration of amines in the technology of a closed cycle of production]. *Tekhnika, enerhetyka, transport APK, 2(97),* 42–47. [in Ukrainian].

ОСОБЛИВОСТІ ПРОЦЕСУ ДИСТИЛЯЦІЇ ДІЕТІЛАМІНУ З ВОДНОГО РОЗЧИНУ ХЛОРИДУ КАЛЬЦІЯ

Дослідження вивчає процес дистиляції діетиламіну ($(C_2H_5)_2NH$) з водних розчинів хлориду кальцію, що має вирішальне значення у процесі виробництва карбонату калію. Незважаючи на важливість фазових рівноваг для системи $CaCl_2 – (C_2H_5)_2NH – H_2O$ для оптимізації процесів дистиляції, у літературі відсутні вичерпні дані, особливо при низьких тисках. Метою даного дослідження є усунення цієї прогалини шляхом вивчення кінетики дистиляції при тисках 47,996, 21,331 та 7,999 кПа. Експериментальні результати показують, що коли вміст хлориду кальцію перевищує 27–28% за масою, температура розчину підвищується, що означає перехід від дистиляції до більш енергоємних процесів через утворення гідратів, таких як $CaCl_2·12H_2O$. Результати підкреслюють, що зниження тиску до 7,999 кПа майже подвоює швидкість дистиляції порівняно з тисками вищими за 21,331 кПа. Була розроблена загальна кінетична модель, що описує взаємозв'язок між водою, що випарувалася, концентрацією діетиламіну, часом процесу і тиском. Ця модель, отримана з кінетики першого порядку, дозволяє точно прогнозувати вміст діетиламіну з часом без прямого врахування змін тиску. Крім того, дослідження підкреслює, що кінетика випаровування води тісно пов'язана з вмістом діетиламіну, оскільки випаровування води значно прискорюється, як тільки концентрація аміну падає нижче за певний поріг. Ці ідеї сприяють розробці ефективних стратегій дистиляції, мінімізації втрат реагентів та оптимізації споживання пари. Отримані рівняння та моделі застосовні не тільки для лабораторних експериментів, але й для масштабування до промислових процесів, пропонуючи практичні інструменти для технологічних розрахунків та підвищення стійкості виробництва карбонату калію.

Ключові слова: мінеральні добрива, карбонат калію, дистиляція, розчин, діетиламін, хлорид кальцію.
Ф. 6. Рис. 8. Табл. 1. Літ. 12.

INFORMATION ABOUT THE AUTHORS

Volodymyr PANASENKO – Candidate of Technical Sciences, Senior Lecturer of the Department of Engineering Mechanics and Technological Processes in the Agro-Industrial Complex at Vinnytsia National Agrarian University (Soniachna St., 3, Vinnytsia, Ukraine, 21008, e-mail: panasenkovv@gmail.com, https://orcid.org/0009-0002-3928-9473).

Dmytro DEINEKA – Candidate of Technical Sciences, Associate Professor of the Department of Chemical Technology of Inorganic Substances, Catalysis, and Ecology at the National Technical University "Kharkiv Polytechnic Institute" (Kyrpychova St., 2, Kharkiv, Ukraine, 61002, e-mail: deynekadn@gmail.com, https://orcid.org/0000-0002-5233-6898).

ПАНАСЕНКО Володимир Володимирович – кандидат технічних наук, старший викладач кафедри інженерної механіки та технологічних процесів в АПК Вінницького національного аграрного університету (вул. Сонячна, 3, м. Вінниця, Україна, 21008, e-mail: panasenkovv@gmail.com, https://orcid.org/0009-0002-3928-9473).

ДЕЙНЕКА Дмитро Миколайович – кандидат технічних наук, доцент кафедри хімічної технології неорганічних речовин, каталізу та екології Національного технічного університету «Харківський політехнічний інститут» (вул. Кирпичова, 2, м. Харків, Україна, 61002, deynekadn@gmail.com, https://orcid.org/0000-0002-5233-6898).