

АНАЛІТИЧНА ХІМІЯ. ФІЗИЧНА ТА КОЛОЇДНА ХІМІЯ.  
НЕОРГАНІЧНА ХІМІЯ. ОРГАНІЧНА ХІМІЯ

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PHASE VAPOR–LIQUID EQUILIBRIUM FOR THE SOLUTIONS  
OF DIMETHYLZINC AND DIMETHYL SELENIDE<https://doi.org/10.23939/ctas2019.02.001>

The paper is devoted to the vapor-liquid equilibrium for solution of dimethylzinc-dimethylselenide. For the description of this equilibrium Wilson's model is proposed. We used data obtained by the tensometric method on the temperature dependence of the saturated vapor pressure for high-purity samples of dimethylzinc, dimethyl selenide and their equimolecular solution. Using the mathematical program package MathCAD 14, the Wilson's model parameters were calculated by the iterative method. On basis of these parameters calculation were provided for the activity coefficients of the solution components, the excess functions of the solution:  $H^E$ ,  $G^E$ , and the "bound energy" as  $TS^E$ . Isothermal P-X diagrams of the state were graphed for the dimethylzinc dimethylselenide system. From these calculations, the following conclusions were made: about the negative deviation of this system from the Raoult's law and about the homogeneity of the solution within the range of all concentrations and temperatures (280–340 K).

**Keywords:** dimethylzinc, dimethyl selenide; solution; saturated vapor pressure; diagram of the state; activity coefficients; azeotrope; excess functions of mixing.

**Introduction**

The practical use of dimethylzinc, dimethyl selenide and their solutions in modern technological processes requires knowledge of reliable thermodynamic parameters of the phase transition from liquid to vapor. The temperature dependence of the saturated vapor pressure for high-purity dimethylzinc, dimethyl selenide and their equimolecular solution, as well as the enthalpy and entropy of the evaporation of these systems, has been determined before [1].

**The purpose of the work** is, according to the tensometric experiment, to calculate the activity coefficients for components, the excess functions of the solution, and to construct isothermal P-X diagrams for the "dimethylzinc-dimethyl selenide" system, which are necessary for quantitative calculations of the solution components separation.

**Materials and methods of research**

The obtaining, purification of dimethylzinc and dimethyl selenide samples and the method of the

tensometric experiment are described in [1,2]. The total content of impurities was determined by a decrease in the melting point [3] and amounted to  $0.03 \pm 0.02$  mol %. According to the results of the gas chromatographic analysis, the dimethyl zinc sample contains 0.01 % by weight of methyl iodide. According to spectral data, the metals impurities content does not exceed  $10^{-4}$  % by weight. According to the gas-liquid chromatography, organic substances impurities were not detected. Taking into account the specific properties of the considered system (high reactivity toward air components, high volatility and toxicity), these substances were kept in hermetically sealed vacuumized ampoules. All of the operations associated with the taking of weighed portions of individual components were also performed under vacuum; thin walled microampoules were filled by means of vacuum distillation, then sealed and weighed. The equimolar solution was prepared by mixing preliminarily selected weights of the initial components (precision of weighing  $\pm 1 \cdot 10^{-4}$  g).

**Results and discussion**

The task of diagram constructing for the state of vapor-liquid equilibrium according to tensometric data is rather complicated, since this method, as a rule, does not allow, in conjunction with the general pressure of saturated vapor, to determine the composition of equilibrium phases. This is particularly difficult in the case of highly volatile, toxic and highly active substances, such as alkyl compounds of zinc and selenium. However, in this case, there is one possible solution to this problem associated with the existence of the azeotrope in the dimethylzinc dimethyl selenide system, the molar fraction of which is 0.5 [1, 4, 5]. Usually, for solving such a problem, with a minimum number of experimental data, can to use semiempirical relations, which must be in agreement with the Gibbs-Duhem equation. Such well-known relationships are the models by Margules and van Laar [6], Skatchard-Hamer [7], and more modern – by Wilson [6,8], NRTL [6], UNIQUAC [6]. The analysis of literature sources [9-16], as well as the experience of our laboratory, in which studies of the vapor-liquid equilibrium of nonideal systems with both positive and negative deviations from the Raoult’s law [17], have allowed us to choose the Wilson’s model. For the binary system the Wilson’s equations are as (1) and (2).

$$\ln(\gamma_1) = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left[ \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right] \quad (1)$$

$$\ln(\gamma_2) = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left[ \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right] \quad (2)$$

In equations (1) and (2), the parameters  $\Lambda_{ij}$  are directly related to the difference in the energy of interaction ( $\lambda_{ij} - \lambda_{ii}$ ) between the pair  $ij$  and the pair  $ii$  according to the equation (3).

$$\Lambda_{ij} = \frac{V_j^L}{V_i^L} \exp \left[ -\frac{\lambda_{ij} - \lambda_{ii}}{RT} \right] \quad (3)$$

where  $V_j^L$ ;  $V_i^L$  – molar volumes of components in liquid state.

To determine the coefficients  $\Lambda_{ij}$ , the data on the composition of the azeotrope ( $x_1 = x_2 = 0.5$ ), the saturated vapor pressure of the azeotrope ( $P_{az}$ ), and the saturated vapor pressure of the individual dimethylzinc and dimethyl selenide ( $P_1^0$ ,  $P_2^0$ ) were used in equations (1) and (2). These pressure values were obtained from the temperature dependence of the saturation vapor pressure (Table 1) for the mentioned systems in the range 273–346 K [1].

Thermodynamic calculations were carried out for temperatures of 280, 300, 320 and 340 K. If we consider the gas phase to be ideal, then for the

azeotropic mixture of content  $x_1 = 0.5$ , we obtain the expression (4) for the activity coefficients.

$$\gamma_i^{az} = \frac{P^{az}}{P_i^0} \quad (4)$$

Table 1

**Results of statistical processing of the primary data on the temperature dependence of the saturated vapor pressure for dimethylzinc, dimethyl selenide and their equimolecular solution**

System	Coefficients in equation $\ln p=A/T + B$		$S_A$	$S_B \cdot 10^2$	$\rho$
	-A	B			
Zn (CH <sub>3</sub> ) <sub>2</sub>	3543	22.723	12	4.2	0.999
Se (CH <sub>3</sub> ) <sub>2</sub>	3697	22.701	10	3.5	0.999
Zn (CH <sub>3</sub> ) <sub>2</sub> · Se CH <sub>3</sub> ) <sub>2</sub>	3946	23.070	22	7.4	0.998

Designation:  $S_A$ ,  $S_B$  – mean square deviation of coefficients A and B for statistics sample,  $\rho$  – linear correlation coefficient.

Table 2 shows the results of calculations of the vapor pressure for individual dimethylzinc and dimethyl selenide ( $P_1^0$ ,  $P_2^0$ ), the saturated vapor pressure for the azeotrope ( $P_{az}$ ), and the activity coefficients of the components in azeotrope ( $\gamma_1^{az}$ ,  $\gamma_2^{az}$ ) at various temperatures.

Table 2

**The saturated vapor pressure for the of dimethylzinc ( $P_1^0$ ), dimethyl selenide ( $P_2^0$ ), the equimolecular azeotropic ( $P_{az}$ ), and the activity coefficients of the components in azeotrope ( $\gamma_1^{az}$ ,  $\gamma_2^{az}$ )**

T, K	$p_1^0$ , κPa	$p_2^0$ , κPa	$p_{az}$ , κPa	$\gamma_1^{az}$	$\gamma_2^{az}$
280	23600	13300	7900	0.3348	0.5940
300	54900	32100	20300	0.3698	0.6324
320	114800	69400	46100	0.4016	0.6643
340	220100	137000	95200	0.4325	0.6949

The equations (1) and (2) will have the forms as (5) and (6), taking into account that at the point of the azotrope  $x_1=x_2=0.5$  and  $\gamma_i=\gamma_i^{az}$  (5)

$$\ln(0.5\gamma_1^{az}) = -\ln(1 + \Lambda_{12}) + \left[ \frac{\Lambda_{12}}{1 + \Lambda_{12}} - \frac{\Lambda_{21}}{\Lambda_{21} + 1} \right] \quad (5)$$

$$\ln(0.5\gamma_2^{az}) = -\ln(1 + \Lambda_{21}) - \left[ \frac{\Lambda_{12}}{1 + \Lambda_{12}} - \frac{\Lambda_{21}}{\Lambda_{21} + 1} \right] \quad (6)$$

The two-parameter equations (5) and (6) were solved for  $\Lambda_{12}$  and  $\Lambda_{21}$  using the mathematical program package MathCAD 14 by the iteration method using the Given-Find block [18, 19]. The results of the calculation of the coefficients  $\Lambda_{12}$  and  $\Lambda_{21}$  at various temperatures are given in Table 3.

Table 3

**The coefficients of the Wilson’s model for solutions of dimethylzinc and dimethyl selenide at various temperatures**

$\Lambda_{ij}$	T=280 K	T=300 K	T=320 K	T=340 K
$\Lambda_{12}$	6.686	6.134	5.716	5.394
$\Lambda_{21}$	1.617	1.398	1.233	1.082

The calculated values of the parameters of the Wilson’s equation ( $\Lambda_{12}$  and  $\Lambda_{21}$ ) allow us to find the dependences for the activity coefficients ( $\gamma_1$ ,  $\gamma_2$ ) – Table 4, partial pressure of components ( $P_1$ ,  $P_2$ ) – Fig. 1, vapor phase composition ( $Y_1$ ) – Fig. 2 and the separation coefficient ( $\alpha$ , relative volatility) – Table 4 from the composition of the solution ( $x_1$ ), to graph isothermal diagrams for vapor-liquid equilibrium state (Fig. 3).

The separation coefficient was calculated by the equation (7).

$$\alpha = \frac{x_2 Y_1}{x_1 Y_2} \quad (7)$$

Table 4

**The activity coefficients of dimethylzinc ( $\gamma_1$ ) and dimethyl selenide ( $\gamma_2$ ) in binary solution and  $\ln(\alpha)$  at various temperatures**

$x_1$	$\gamma_1$			
	280 K	300 K	320 K	340 K
1	2	3	4	5
0.1	0.1110	0.1417	0.0310	0.2047
0.2	0.1494	0.1816	0.0846	0.2458
0.3	0.1977	0.2313	0.1738	0.2959
0.4	0.2584	0.2929	0.3119	0.3572
0.5	0.3263	0.3698	0.5000	0.4324
0.6	0.4311	0.4657	0.7064	0.5250
0.7	0.5527	0.5852	0.8729	0.6378
0.8	0.7044	0.7311	0.9644	0.7714
0.9	0.8799	0.8941	0.9954	0.9137
1.0	1.0000	1.0000	1.0000	1.0000
$x_1$	$\gamma_2$			
	280 K	300 K	320 K	340 K
0.0	1.0000	1.0000	1.0000	1.0000
0.1	0.9833	0.9864	0.9885	0.9903
0.2	0.9329	0.9438	0.9518	0.9586

Continuation of Table 4

1	2	3	4	5
0.3	0.8494	0.8705	0.8865	0.9008
0.4	0.7349	0.7659	0.7906	0.8134
0.5	0.6091	0.6323	0.6642	0.6948
0.6	0.4352	0.4760	0.5117	0.5472
0.7	0.2730	0.3101	0.3444	0.3797
0.8	0.1303	0.1574	0.1840	0.2127
0.9	0.0354	0.0484	0.0627	0.0791
$x_1$	$\ln(\alpha)$			
	280 K	300 K	320 K	340 K
0.0	–	–	–	–
0.1	-1.608	-1.404	-1.246	-1.103
0.2	-1.258	-1.111	-0.995	-0.887
0.3	-0.884	-0.789	-0.712	-0.639
0.4	-0.472	-0.425	-0.386	-0.349
0.5	0.000	0.000	0.000	0.000
0.6	0.564	0.515	0.473	0.433
0.7	1.279	1.172	1.080	0.993
0.8	2.261	2.073	1.912	1.763
0.9	3.788	3.452	3.172	2.921
1.0	–	–	–	–

The thermodynamic analysis for the vapor-liquid equilibrium is considered to be more complete if the excess functions of the solutions formation are calculated: enthalpy ( $H^E$ ), Gibbs energy ( $G^E$ ), and “bound energy” ( $TS^E$ ). Many authors in various publications [6, 17, 20–24] argue that using temperature dependence of vapor pressure over a solution it is possible to calculate these excess functions, although calculated ones may differ somewhat from the values obtained by direct methods. In their opinion, according to these data it is possible to estimate the values of the parameters, to determine their sign and to characterize the tendencies of changing the thermodynamic characteristics of the investigated solutions. We have used this opportunity also because Wilson’s model allows to make these calculations so easy. For binary solution the excess heat of mixing was calculated by the equation (8).

$$H^E = x_1 \frac{x_2 \Lambda_{12}}{x_1 + \Lambda_{12} x_2} (\lambda_{12} - \lambda_{11}) + x_2 \frac{x_1 \Lambda_{21}}{x_2 + \Lambda_{21} x_1} (\lambda_{12} - \lambda_{22}) \quad (8)$$

At slight change in temperature the values ( $\lambda_{ij} - \lambda_{ii}$ ), which are in equation (8), can be considered as constants [6]. These values can be calculated using temperature dependence (3) for the coefficients ( $\Lambda_{12}$  and  $\Lambda_{21}$ ) of the Wilson’s equation. Table 5 presents the results of the statistical processing of the data for the temperature dependence of these coefficients  $\Lambda_{12}$  and  $\Lambda_{21}$ , which were approximated by the equations of straight lines as well as gives calculations ( $\lambda_{12} - \lambda_{11}$ ) and ( $\lambda_{12} - \lambda_{22}$ ).

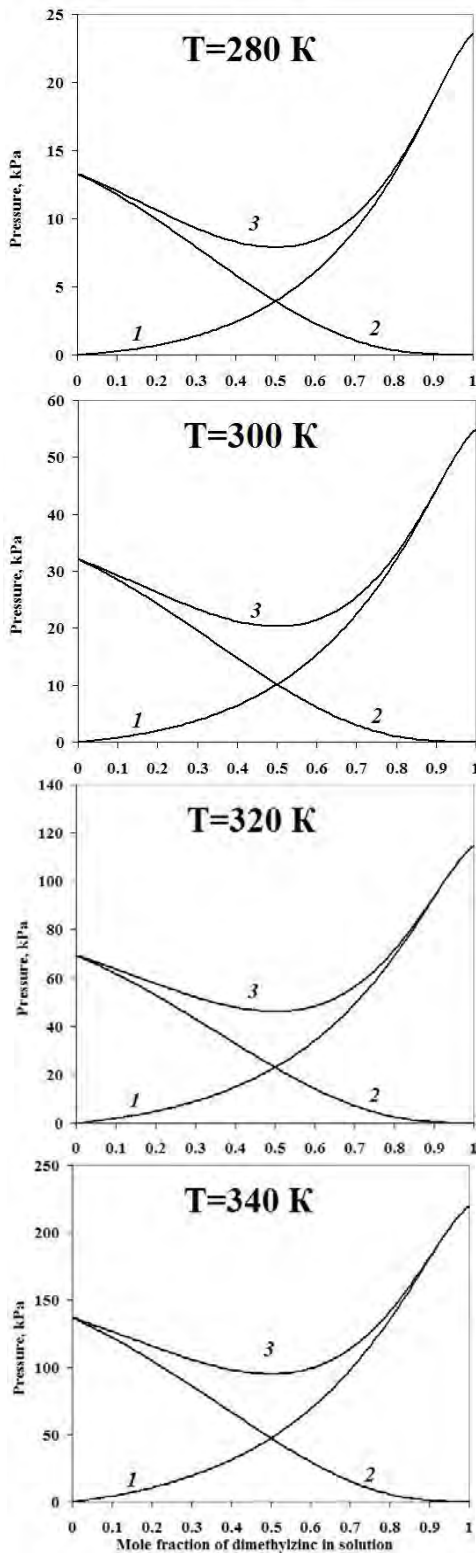


Fig. 1. The dependence of the partial pressures of components ( $P_1$ ,  $P_2$ ) on the content of dimethylzinc ( $x_1$ ) in the binary solution of dimethylzinc-dimethyl selenide at various temperatures:

1 –  $Zn(CH_3)_2$ ; 2 –  $Se(CH_3)_2$ ; 3 – total pressure

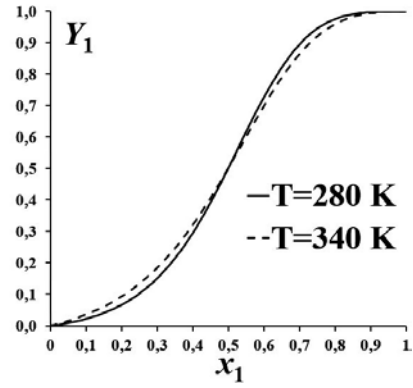


Fig. 2. The dependence of the vapor phase composition ( $Y_1$ ) on the content of dimethylzinc ( $x_1$ ) in the binary solution of dimethylzinc and dimethyl selenide at various temperatures

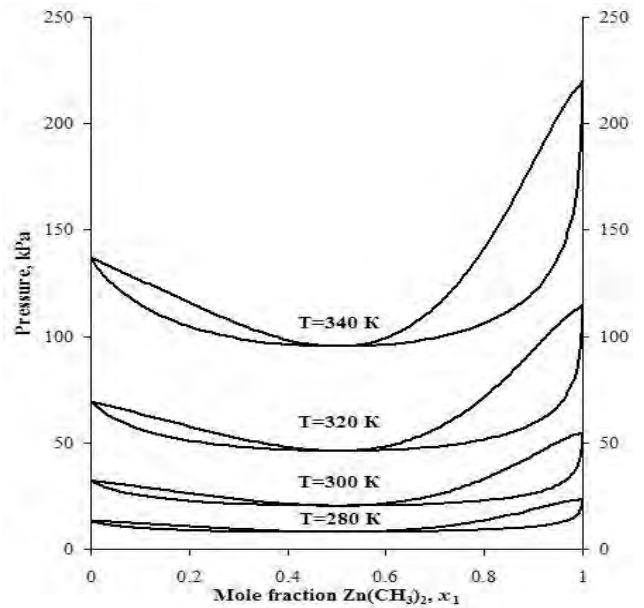


Fig. 3. Isothermal diagrams for vapor-liquid equilibrium state of the system such as dimethylzinc- dimethyl selenide

The excess Gibbs energy ( $G^E$ ) and the excess energy of the solution ( $TS^E$ ) were calculated by equations (9) and (10)

$$G^E = RT(x_1 \ln(\gamma_1) + x_2 \ln(\gamma_2)) \quad (9)$$

$$TS^E = H^E - G^E \quad (10)$$

Table 5

Temperature dependence of parameters  $\Lambda_{12}$  and  $\Lambda_{21}$  in Wilson's model

$\ln\Lambda_{12} = A/T + B$				
A	B	$S_A$	$S_B$	$\rho$
1	2	3	4	5
341.1	0.6795	7.30	0.0237	0.999
$(\lambda_{12} - \lambda_{11}) = -2836 \pm 193, \text{ J/mole}$				
$\ln\Lambda_{21} = A/T + B$				

Continuation of Table 5

1	2	3	4	5
A	B	$S_A$	$S_B$	$\rho$
632.9	-1.776	16.4	0.0532	0.998
$(\lambda_{12} - \lambda_{22}) = -5262 \pm 433, \text{ J/mole}$				

Designation:  $S_A$ ,  $S_B$  – mean square deviation of coefficients A, B for statistics sample;  $\rho$  – correlation coefficient.

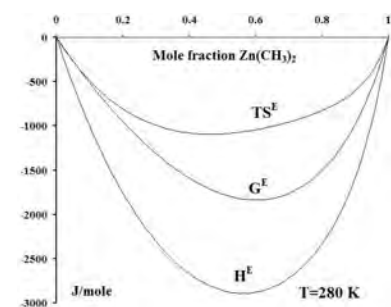


Fig.4 Comparison of excess functions dependences on the content of dimethylzinc ( $x_1$ ) at a temperature of 280K in binary solution dimethylzinc-dimethyl selenide

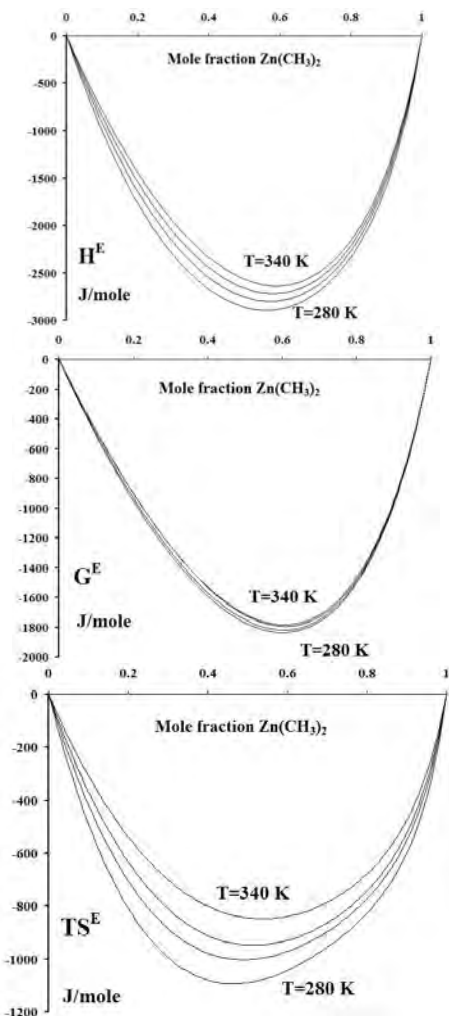


Fig. 5. Dependences of excess functions on the content of dimethylzinc ( $x_1$ ) at different temperatures in binary solution dimethylzinc-dimethyl selenide

The results of the calculation of excess functions such as  $H^E$ ,  $G^E$  and  $TS^E$  are shown in Fig. 4 and Fig. 5.

## Conclusions

In this work the thermodynamic parameters of the vapor-liquid equilibrium system of dimethylzinc dimethylselen are calculated from the tensometric data obtained for high-purity dimethylzinc, dimethyl selenide and for their equimolecular solution. For this purpose, the Wilson's model was used and the model's parameters were calculated by the activity coefficients of components in the azeotrope. The calculation was carried out using the mathematical package MathCad 14. The Wilson's model parameters allowed to calculate the activity coefficients of the components, the excess solution functions, and to graph isothermal  $P$ - $X$  state diagrams. The values of the activity coefficients ( $\gamma_i < 1$ ), the excess enthalpy of the solution ( $H^E < 0$ ), and the shape of isothermal  $P$ - $X$  equilibrium diagrams indicate the existence of an azeotrope in this system and the negative deviation of this solution from the ideal. The value of excess Gibbs energy of this solution ( $G^E$ ) in the whole range of concentrations and temperatures is negative and that indicates the formation of homogeneous solutions. As the temperature rises, then excess enthalpy increases and that indicates a positive value of the change in heat capacity during the solution formation of the dimethylzinc-dimethyl selenide.

The deviation of this system from Raoult's law is explained by the enthalpy factor in our opinion. In the investigated solution the energy of interaction between different molecules is greater than that between identical molecules. Significant difference between the parameters  $(\lambda_{12} - \lambda_{11})$  and  $(\lambda_{12} - \lambda_{22})$  in the Wilson's equation indicates about that.

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#### ФАЗОВА РІВНОВАГА ПАРА-РІДИНА РОЗЧИНІВ ДИМЕТИЛЦИНКУ ТА ДИМЕТИЛСЕЛЕНУ

Розглянуто парорідинну рівновагу розчину диметилцинк-диметилселен. Для опису цієї рівноваги запропоновано модель Вільсона. Використано дані щодо температурної залежності тиску насиченої пари високочистих зразків диметилцинку, диметилселену та їх еквімолекулярного розчину, отриманих тензіметричним методом. Застосовуючи математичний пакет програм Mathcad 14, методом ітерацій розраховано параметри моделі Вільсона. На основі цих параметрів пораховано коефіцієнти активності компонентів розчину, надлишкові функції розчину:  $H^E$ ,  $G^E$ , "зв'язана енергія"  $TS^E$ . Побудовано ізотермічні P-X діаграми стану системи диметилцинк-диметилселен. За результатами розрахунків зроблено висновки: про від'ємне відхилення даної системи від закону Рауля та про гомогенність розчину в усьому інтервалі концентрацій та температур (280–340 K).

Ключові слова: диметилцинк, диметилселен; розчин; тиск насиченої пари; діаграма стану; коефіцієнти активності; азеотроп; надлишкові функції змішування.