METHOD FOR OBTAINING ISOTHERMAL DIAGRAMS OF THE LIQUID − VAPOR EQUILIBRIUM FOR THE SYSTEM AS DIMETHYL ZINC − DIMETHYL TELLURIDE

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Abstract. According to the obtained experimental temperature dependences of the saturated vapor pressure on dimethylzinc – dimethyltelluride solutions with dimethylzinc content of 50.0 and 70.32 mol. %, isothermal sections (280, 290, 300, 310, and 320 K) were made. For the dimethylzinc – dimethyltelluride system based on a limited set of experimental data for the "liquid-vapor" equilibrium, the vapor composition was calculated according to the Duhem – Margules equation, as well as the partial pressures and the distribution coefficient.

Keywords: diagrams of state, liquid-vapor equilibria, dimethyl zinc – dimethyl telluride, vapor pressure.

1. Introduction

Thermodynamic characteristics of solutions are important parameters, both for the theoretical explanation of the features of the solution components interaction and for practical application in the processes of production and purification of substances. These characteristics can be obtained by direct measurement of necessary parameters such as mixing enthalpy,[1,2] and excess volumes[3] or calculated on the basis of liquid-vapor equilibrium data using the Duhem-Margules equation or local composition models.[4-6]

This work is a continuation of a series of works on the study of liquid-vapor equilibrium in binary organometallic systems. Previously,[7-10] based on the results of the temperature dependence of the saturated vapor pressure on equimolecular solutions of dimethylzinc-dimethylselenium and dimethyltelluride-dimethylcadmium in the range of 280-340 K, we established that the specified systems in the liquid phase manifest themselves as single components, which completely dissociate into their component substances during the transition into the gas phase, which indicates the presence of an azeotrope (at x=0.5). We used the Wilson model to describe the liquid-vapor equilibrium in these systems. Using the mathematical software package MathCAD, the parameters of the Wilson model were obtained by the iteration method, based on which the activity coefficients of the solution components and the excess functions of the solution were calculated, and isothermal *P-X* diagrams were constructed for the dimethylzinc-dimethylselenium[7] and dimethyltelluride-dimethylcadmium[8] systems.

The purpose of this work is to construct isothermal *P-X* diagrams of the state of the dimethylzinc-dimethyltelluride on the basis of a limited set of tensimetric experimental data.

2. Experimental

2.1. Materials

The method of obtaining dimethylzinc (boiling point 319 K) and dimethyl telluride (boiling point 355 K) is described in the literature[11] and these substances were purified by the method of rectification under reduced pressure. The total impurities content was 0.03±0.02 mol. %, which was determined by decreasing the melting point. According to spectral data, the content of metal impurities does not exceed 10^{-4} % by mass. According to gas-liquid chromatography, organic substances impurities were not detected. Taking into account the specificity of these substances, in particular, their interaction with air oxygen, as well as high reactivity, volatility, and toxicity, they were stored in hermetically sealed vacuumed ampoules. All operations related to taking a certain mass of individual organic elemental compounds were also carried out under a vacuum. These masses were placed into thin-walled micro ampules by the vacuum distillation method, then sealed and weighed with accuracy $\Delta m = \pm 1 \cdot 10^{-2}$ mg. The solutions were prepared by mixing previously selected amounts of the initial components.

2.2. Tensiometric Measurements

The temperature dependence of the saturated vapor pressure for the substances was determined by the static method with a membrane zero pressure gauge. A detailed

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description of the experimental setup is given in the work.[12] The accuracy of temperature and pressure measurements is 0.1 K and 130 Pa, respectively. The reliability of the work of the tensiometric installation was verified in a series of experiments on measuring the temperature dependence of the saturated vapor pressure of pentane, hexane, and heptane,[10] and the results of the tensimetric experiments were compared with literature data.[13] A comparative analysis of our and the literature data was carried out using the ANOVA method,[14] which showed that our data and literature ones do not differ within experimental error.

3. Results and Discussion

The parameters of temperature dependence for saturated vapor pressure (Table 1) according to Eq. (1) for dimethylzinc and dimethyltelluride were taken from works,[7,11] respectively.

$$ln\ p = A/T + B \qquad (1)$$

A series of experiments was also conducted to determine the temperature dependence of saturated and unsaturated vapor pressure on different concentrations of dimethylzinc – dimethyltelluride solutions, the dimethylzinc content of which was 50.00 and 70.32 mol. %, respectively. The primary data of the obtained temperature dependences were published in [10]. These dependencies are approximated by linear Eq. (1) for saturated vapor and by Eq. (2) for unsaturated vapor and they are shown in Tables 2 and 3 according to the work.[10]

$$P = CT + D \qquad (2)$$

It should be noted that in work[10] the coordinates (temperature and pressure) are defined for the experiment moments which are corresponding to the complete evaporation of the liquid in the tensiometer: (305.0 K; 10787 Pa), (309.7 K; 15502 Pa), (309.3 K; 15818 Pa), (352.2 K; 80584 Pa). The coordinates of these points are on the vapor line of the corresponding isothermal diagram. The tensiometric method, as a rule, does not make it possible to directly determine the composition of the equilibrium phases together with the total vapor pressure. It is especially difficult to do this when working with highly volatile, reactive, and toxic substances, such as alkyl compounds of zinc and tellurium. It should be noted that unlike equimolecular solutions of dimethylzinc – dimethylselenium,[7] dimethyltelluride-dimethylcadmium,[8] diethylzinc – diethylselenium,[9] for which the formation of an azeotrope is observed, the equimolecular system dimethylzinc – dimethyltelluride is bivariate,[10] *i.e.*, the saturated vapor pressure depends on the mass of the solution that evaporates in the closed volume of the tensiometer. Therefore, using tensiometric data, the method of calculating activity coefficients according to Wilson's equations, which is suitable for calculation in the case of an azeotrope,[7] cannot be used for the dimethylzinc – dimethyltelluride system, where the formation of an azeotrope was not observed.

Table 1. Parameters of the temperature dependence of pressure (Pa) on unsaturated vapor of dimethylzinc and dimethyltelluride according to Eq. (1)

Substance index	System	The coefficients of equation $ln\ p = A/T + B$		S_A	$S_B \cdot 10^2$	R^2	References
		$-A$, K	B				
(1)	Zn(CH$_3$)$_2$	3543	22.723	12	4.2	0.9998	[7]
(2)	Te(CH$_3$)$_2$	3962	22.224	-	-	-	[11]

Table 2. Parameters of the temperature dependence of pressure (Pa) on unsaturated vapor of dimethylzinc and dimethyltelluride solutions[10]

Mass of the solution, m, gram	The coefficients of equation $ln(P) = A/T + B$		S_A	$S_B \cdot 10^2$	R^2
	$-A$, K	B			
equimolecular solutions					
0.01244	1894	15.512	125.5	42.4	0.9956
0.01717	2481	17.658	73.9	24.7	0.9999
0.08588	3042	19.809	17.3	5.7	0.9997
0.16225	3225	20.469	19.3	6.0	0.9999
0.26614	3392	21.078	10.9	3.6	0.9999
0.27530	3556	21.565	21.6	7.1	0.9997
0.45918	3326	20.995	9.3	3.1	0.9999
solutions with a dimethylzinc content of 70.32 mol. %					
0.01804	2626	18.158	101	35	0.9941
0.08102	2629	18.761	37.1	12.0	0.9980
0.26925	3108	20.666	33.4	10.9	0.9990

Table 3. Parameters of the temperature dependence of pressure (Pa) on unsaturated vapor of dimethylzinc and dimethyltelluride solutions[10]

Mass of the solution, m, gram	The coefficients of equation $P=CT + D$		S_A	$S_B \cdot 10^2$	R^2
	C, Pa/K	$-D$, Pa			
equimolecular solutions					
0.01244	52.81	5196	2.51	829	0.993
0.01717	62.93	3987	3.62	1253	0.993
solutions with a dimethylzinc content of 70.32 mol. %					
0.01804	63.62	3860	3.81	1270	0.986
0.08102	263.7	12291	21.4	7653	0.994

Table 4. Calculated pressure values according to approximation Eq. (1) for the content of dimethylzinc in the solution of 50.00 mol. %and 70.32 mol. %, using parameters from Table 2

T, K	Pressure (Pa) in the tensiometer for the mass of the solution (m, mg)									
	50.00 mol. % $Zn(CH_3)_2$							70.32 mol. % $Zn(CH_3)_2$		
	12.44	17.17	85.88	162.25	266.14	275.30	459.18	18.04	81.02	269.25
270	4901	4765	5127	5037	4989	4423	5863	4592	8300	9461
280	6296	6616	7667	7717	7814	7080	9104	6499	11751	14271
290	7950	8981	11152	11479	11866	10970	13712	8981	16244	20926
300	9884	11944	15820	16631	17524	16509	20097	12145	21975	29912
310	12116	15596	21941	23524	25237	24198	28738	16107	29154	41781
320	14665	20028	29814	32561	35525	34631	40185	20989	38001	57154
330	17546	25332	39768	44191	48982	48496	55062	26915	48744	76712
340	20773	31601	52153	58906	66272	66581	74061	34012	61614	101197
350	24357	38926	67344	77243	88130	89769	97943	42410	76847	131400
360	28308	47398	85734	99774	115356	119041	127531	52237	94677	168159

A technique is proposed[6] that allows determining the composition of the liquid and vapor phases at a certain temperature. In particular, in order to determine the pressure that characterizes one of the points of the liquid line on the **P-X** diagram, it is necessary to examine the sample, which should be so large that the evaporation of a solution part does not noticeably change the solution composition. Due to the uncertainty of the assessment statement "so large" and the impossibility in a real thesimetric experiment to significantly increase the volume of the liquid phase, the saturated vapor pressure measurements were carried out for each solution several times with various masses of the solution in the temperature range of 270-360 K (Table 3). Using the obtained dependences, the saturated vapor pressure of solutions was calculated at various temperatures of this range with a step of 10 degrees according to approximation equations (1) for the content of dimethylzinc in the solution of 50 and 70 mol %. There are calculation results in Table 4.

The isothermal dependences between the mass of the solution (m, mg) and the pressures P, which were calculated according to Eq. (1) and shown in Table 4, were approximated according to the semi-logarithmic Eq. (3):

$$ln(P) = \frac{E}{m} + F \tag{3}$$

The appropriateness of choosing Eq. (3) for these approximations is confirmed by the satisfactory correlation coefficient values (R), which are given in Table 5, as well as by the physical meaning that when the mass of the solution in the tensiometer increases, the logarithm of the total vapor pressure goes towards $F = ln(P_{LIMIT})$.

According to the results of the model, at an infinitely large amount of solution (m) the pressure limit values as P_{LIMIT} were found. The natural logarithms for P_{LIMIT} value is equal to the intercept F in Eq. (3). These pressure values (P_{LIMIT}) correspond to points on the liquid line. Table 5 gives the values of slopes E, intercepts F and squares of correlation coefficients, as well as P_{LIMIT} values corresponding to points on the liquid line for equimolar solutions and for solutions with a dimethylzinc content of 70.32 mol. %. For slopes E and intercepts F the temperature dependences, which are well described by linear correlations, are shown in Fig. 1 (a and b) for equimolar solutions, as well as in Fig. 2 (a and b) for solutions with a dimethylzinc content of 70.32 mol. %.

Table 5. Parameters of Eq. (3) of the relations between the solutions weight (**m**, mg) with the dimethyl zinc content of 50.00 mol. % and 70.32 mol. % and the calculated pressures P for various temperatures (**T**)

T, K	The coefficients of equation $ln(P) = \dfrac{E}{m} + F$		R	P_{LIMIT}, Pa	The coefficients of equation $ln(P) = \dfrac{E}{m} + F$		R	P_{LIMIT}, Pa
	$-E$	F			$-E$	F		
	equimolecular solutions				solutions with a 70.32 mol. % of $Zn(CH_3)_2$			
270	0.67825	8.53313	0.254	5080	13.89868	9.20151	0.999	9912
280	3.07761	8,98527	0.805	7985	14.73698	9.59023	0.997	14621
290	5.31149	9.40623	0.933	12164	15.51747	9.95213	0.990	20997
300	5.89212	9.80155	0.852	18062	18.36095	10.43454	0.991	34015
310	10.85122	10.16423	0.965	25958	14.81235	10.46127	0.844	34936
320	11.17543	10.51124	0.984	36726	17.56625	10.90214	0.966	54292
330	12.89315	10.83492	0.986	50763	18.16640	11.18042	0.958	71713
340	16.07224	11.15251	0.984	69739	23.54880	11.47913	0.975	96676
350	16.03413	11.42681	0.988	91749	19.26381	11.68929	0.944	119287
360	17.47374	11.69810	0.988	120342	19.76679	11.92252	0.937	150620
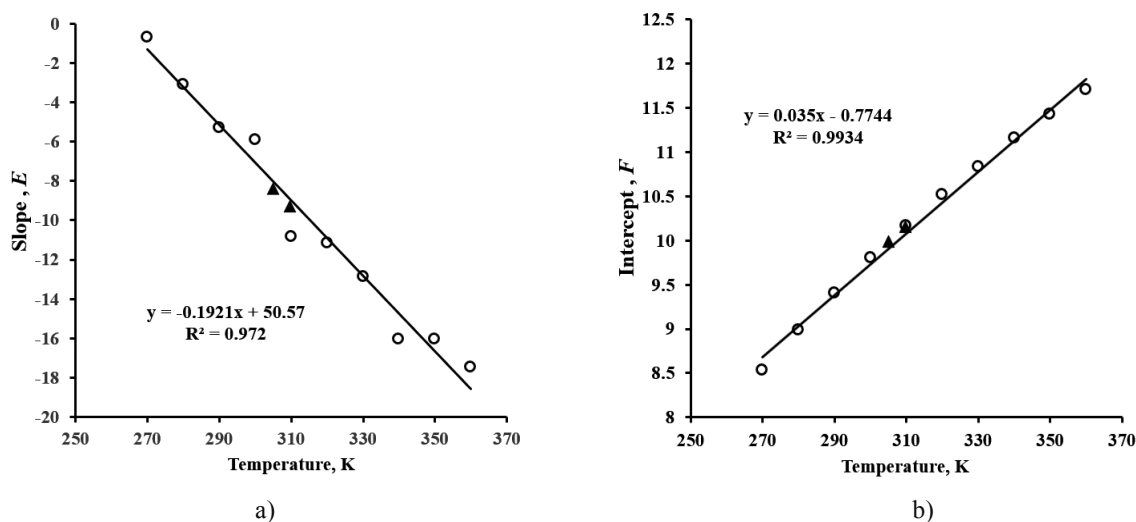
Fig. 1. Temperature dependences for equimolar solutions: **a)** slopes E; **b)** intercepts F in Eq. (3). The triangles indicate the temperatures that correspond to the moments of complete evaporation of the respective solution mass
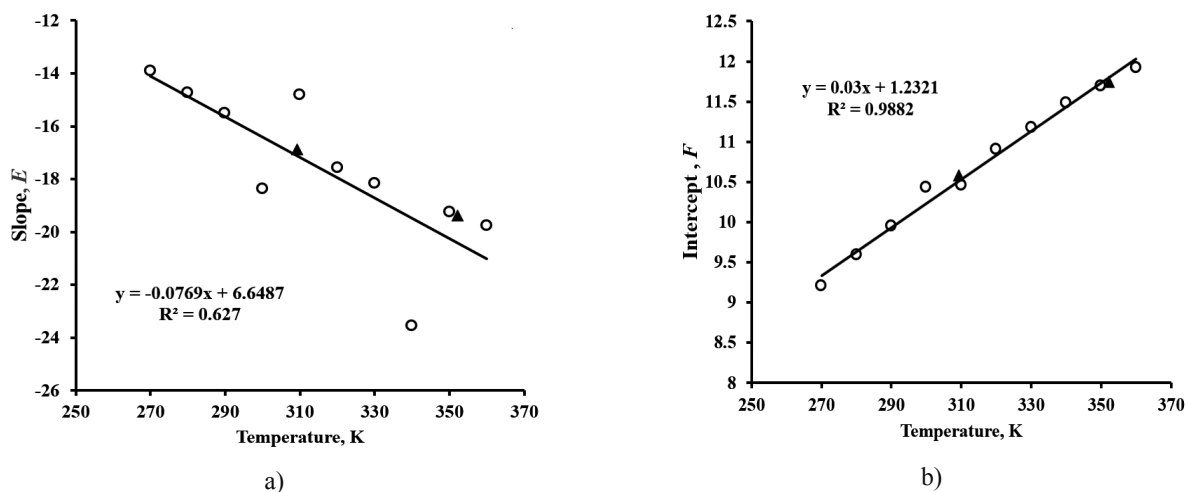
Fig. 2. Temperature dependences for solutions with a dimethylzinc content of 70.32 mol. %: **a)** slopes E; **b)** intercepts F in Eq. (3). The triangles indicate the temperatures that correspond to the moments of complete evaporation of the respective solution mass

Parameters of linear correlations for slopes E and intercepts F with temperature are given in Table 6.

The straight-line temperature dependences of the intercept F for solutions with a dimethylzinc content of 50.00 mol. % and 70.32 mol. % have similar parameters, however, when moving to the inverse temperature (Table 7), the correlation coefficients increase slightly.

Using Eq. (4) with parameters given in Table 7, Fig. 3 (a and b) shows the temperature dependence of the limit pressure P_{LIMIT}.

$$F(T) = ln(P_{LIMIT}) = \frac{A}{T} + B \qquad (4)$$

Fig. 4 shows a comparison of the temperature dependences of the saturated vapor pressure for individual substances and the limit pressure of P_{LIMIT}, corresponding to the points on the liquid line, for solutions with a dimethylzinc content of 50.00 mol. % and 70.32 mol. %. It should be noted that the calculated total limit pressure increases with an increase in the dimethylzinc content.

Table 6. Parameters of linear correlations for slopes $E(T)$ and intercepts $F(T)$ with temperature

Zn (CH$_3$)$_2$ (mol. %)	Correlation equation	R^2
50.00	$E(T) = -0.1921T + 50.57$	0.972
70.32	$E(T) = -0.0769T + 6.6487$	0.627
50.00	$F(T) = 0.035T - 0.7744$	0.993
70.32	$F(T) = 0.029998T + 1.2321$	0.988

Table 7. Parameters of the temperature dependence of the limit pressure – P_{LIMIT} (Pa) on the saturated vapor over dimethylzinc and dimethyltelluride solutions according to Eq. (4)

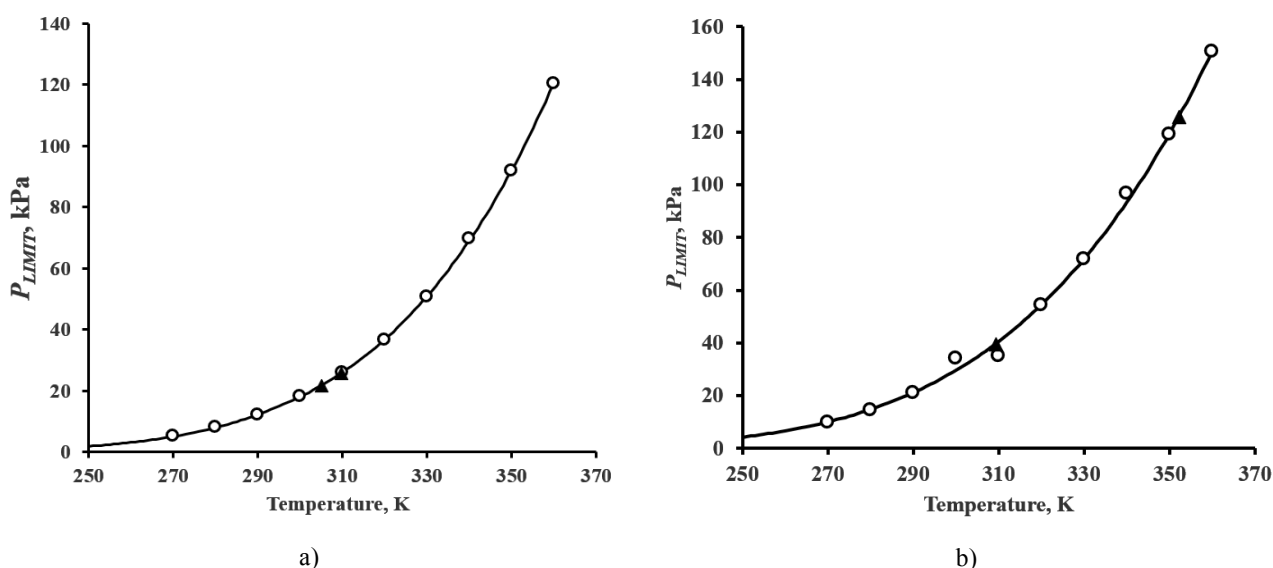| Content Zn (CH$_3$)$_2$, mol. %	The coefficients of Eq. (4)		S_A	$S_B \cdot 10^2$	R^2
	$-A$	B			
50.00	3422	21.206	4.67	1.50	0.99999
70.32	2932	20.067	79	0,25	0.99427

a)

b)

Fig. 3. Temperature dependence of the limit pressure P_{LIMIT} corresponding to points on the liquid line: *a)* equimolar solutions; *b)* for solutions with a dimethylzinc content of 70.32 mol. %. Triangles mark the points that correspond to the temperatures at the moment of complete evaporation of the liquid.
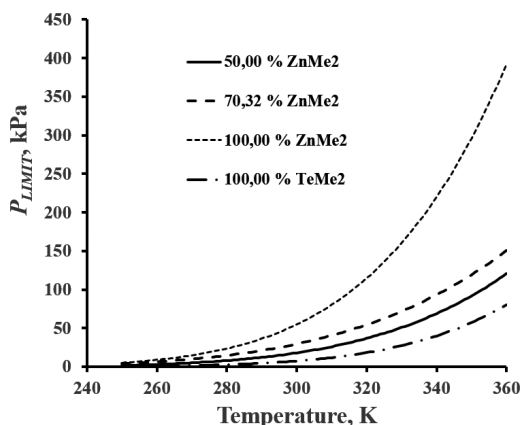
Fig. 4. Comparison of the temperature dependence of the limit pressure P_{LIMIT} corresponding to the points on the liquid line for solutions with dimethylzinc content of 50.00 % and 70.32 mol. % with the dependencies for individual substances

For the "vapor-liquid" equilibrium of the "dimethylzinc – dimethyl telluride" solutions, two points on the liquid line for each temperature were calculated as P_{LIMIT} for the dimethylzinc content of 50.00 mol. % and 70.32 mol. %. Note that the greatest deviation of experimental points from linear correlations for $E(T)$ slopes are observed for the following three temperatures: 300, 310, 340 K (Fig. 1*a* and Fig. 2*a*). To construct liquid lines at a certain temperature (T), a power function was used according to Eqs. (5-7):

$$P = K + L \cdot x_1^{N} \tag{5}$$

$$K = P_2(T, x_2 = 1) \tag{6}$$

$$L = P_1(T, x_1 = 1) - P_2(T, x_2 = 1) \tag{7}$$

The pressures P_1 and P_2 for dimethylzinc and dimethyl telluride, respectively, were calculated according

to Eq. (1) with the parameters of Table 1. In Eq. (5) the power index N was determined by the method of least squares for the one-parameter Eq. (8) at two points $x_1=0.5$ and $x_1= 0.7032$, for which P was equal to P_{LIMIT}.

$$ln\left(\frac{P-K}{L}\right) = N \cdot ln\left(x_1\right) \tag{8}$$

Note that since the logarithmic and exponential functions are very sensitive to the corresponding parameters of these functions, therefore, in order to ensure statistical reliability and avoid significant errors in further calculations, the pressure of P_{LIMIT} was obtained according to Eq. (4), the parameters of which are given in Table 7. Statistically reliable values of P_{LIMIT} are given in Table 8. The initial data for calculating the parameters of the liquid lines according to the power function (5) and the obtained parameters of these liquid lines are given in Table 8. Note that the difference in the values of N in Eq. (5), which are obtained on the basis of the initial data from Table 5, and N^*, calculated on the basis of statistically reliable values of P_{LIMIT} (Table 8), is negative in most cases and the absolute values as ΔN are within 0.0023-0.0071. However, for three temperatures: 300, 310, and 340 K, the absolute values of ΔN are significantly higher and amount to 0.1157, 0.1364, and 0.0646, respectively.

On the basis of these results, for further calculations we used the value of the power index N^*, which was obtained taking into account statistical analysis. The temperature dependence of the power index N^* in Eq. (5) is well described by a two-parameter linear correlation equation, the parameters of which are given in Table 9 for 14 values temperatures in the range of 270-360 K. When moving from using the initial data from Table 5 to the initial data from Table 8, the square of the correlation coefficient increases from R^2=0.9780 to R^2=0.9993.

Table 8. Initial pressure data (Pa) for calculating parameters of Eq. (5) for liquid lines

T, K	$P_1(T)$	$P_2(T)$	P_{LIMIT} x_1=0.5000	P_{LIMIT} x_1=0.7032	L, Pa	N according to Table 5	N^*	ΔN
270	14776	1901	5074	9974	12876	1.8802	1.8779	-0.0023
280	23610	3210	7979	14700	20400	2.0038	2.0011	-0.0026
290	36525	5229	12161	21092	31296	2.1274	2.1244	-0.0030
300	54885	8245	18022	29545	46640	2.1327	2.2483	0.1157
310	80336	12624	26037	40495	67712	2.5102	2.3737	-0.1364
320	114820	18821	36763	54421	95999	2.5058	2.5013	-0.0045
330	160594	27390	50833	71837	133204	2.6367	2.6317	-0.0051
340	220226	38990	68961	93290	181237	2.7012	2.7658	0.0646
350	296601	54394	91937	119355	242207	2.9109	2.9045	-0.0064
360	392909	74492	120625	150626	318417	3.0560	3.0489	-0.0071
305.0	66610	10238	21727	34679	56372	2.3145	2.3108	-0.0037
309.7	79451	12469	25760	40126	66982	2.3739	2.3699	-0.0040
309.3	78284	12264	25395	39637	66020	2.3688	2.3649	-0.0039
352.2	315961	58379	97727	125767	257582	2.9423	2.9358	-0.0065

Fig. 5 shows the temperature dependence for the N^* degree in Eq. (3) when applying the initial data from Table 8.

Table 10 shows the deviation of the experimental points for P_{LIMIT} (Table 5) from the calculated values according to the model Eq. (5) for the liquid line.

Fig. 6 (*a* and *b*) shows, respectively, the temperature dependence of absolute ΔP_{LIMIT} (kPa) and relative – δP_{LIMIT} (% of the experiment) deviation for the experimental points of P_{LIMIT} (Table 5) from the calculated values according to the model Eq. (5) for the liquid line.

As the temperature increases, the deviation of calculated values from the experimental points P_{LIMIT} (Fig. 9) changes their sign in the temperature range of 300-310 K and significantly increases after the temperature of 310 K. If we consider the patterns of changes in the relative (% of the experiment) deviation δP_{LIMIT} (Fig. 6*b*), then for the studied temperature range, the minimum of this value is observed at a temperature of 300 K, and the maximum value does not exceed 30 %. The ratio $\beta = \delta P_{LIMIT}(0.7)/\delta P_{LIMIT}(0.5)$ between these relative deviations for dimethylzinc concentrations of 70.32 and 50.00 mol. % is in a narrow range from 4.24 to 4.32 (Fig. 7).

Table 9. Parameters of linear correlation equations for the temperature dependence of the power index N in Eq. (5)

Initial data for calculation of N are taken from the tables	The coefficients of equation $N(T) = aT + b$		$S_a \cdot 10^4$	S_b	R^2
	a	$-b$			
Table 5	0.0130	1.6420	5.6	0.18	0.9780
Table 8	0.0130	1.6436	1.0	0.03	0.9993

Table 10. Deviation of the experimental points for P_{LIMIT} (Table 5) from the calculated values according to the model Eq. (5) for the liquid line

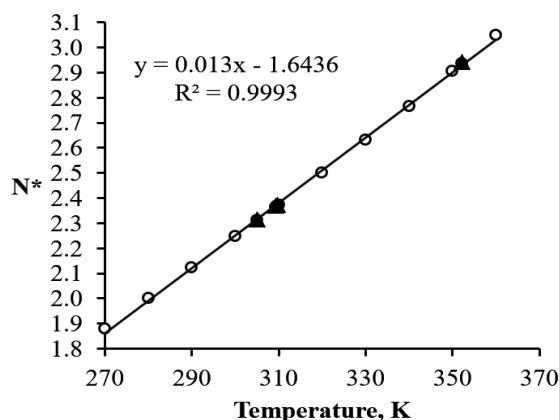| T, K	P_{LIMIT} calculated according to Eq. (5) for x_1		ΔP_{LIMIT} for x_1	
	0.5000	0.7032	0.5000	0.7032
270	5404	8548	-330	1426
280	8306	13294	-327	1406
290	12407	20041	-246	1051
300	18061	29377	-39	168
310	25689	41979	348	-1484
320	35776	58610	987	-4189
330	48883	80122	1950	-8285
340	65638	107428	3323	-14138
350	86742	141496	5195	-22141
360	112968	183324	7657	-32698

Fig. 5. The temperature dependence of the N* degree in Eq. (3) for the liquid line (triangles indicate the temperatures that correspond to the moments of complete evaporation of the solution mass according to Table 2)
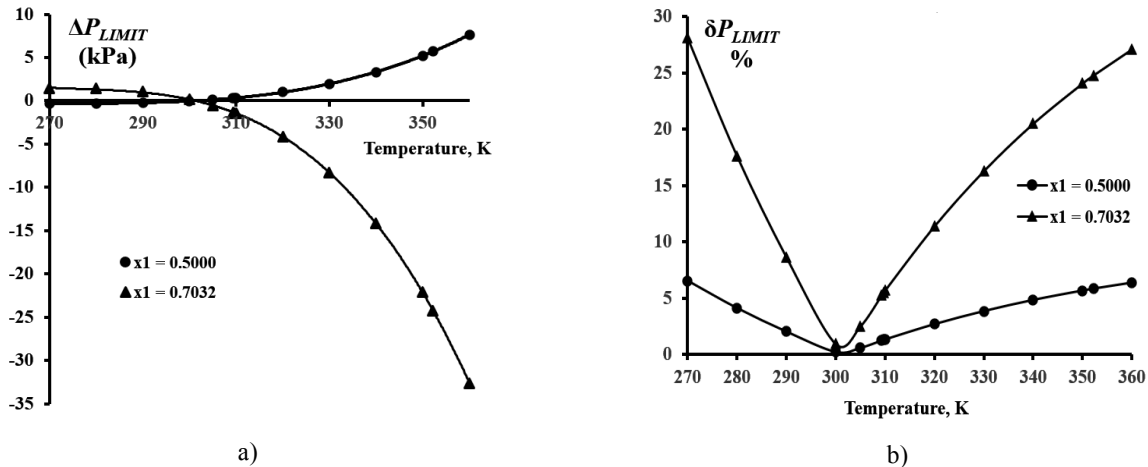
a)

b)

Fig. 6. Temperature dependences of the P_{LIMIT} deviation of the experimental points (Table 5) from the calculated values according to the model Eq. (3) for the liquid line: *a)* absolute deviations (kPa); *b)* relative deviations (%)
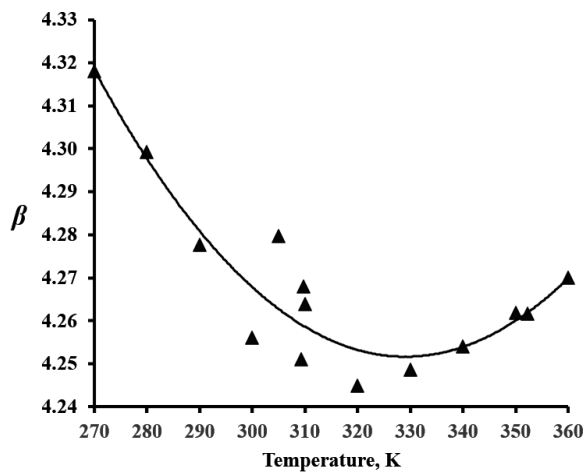

Fig.7. Temperature dependence of the ratio $\beta=\delta P_{LIMIT}(0.7)/\delta P_{LIMIT}(0.5)$ between relative deviations for dimethylzinc concentrations of 70.32 and 50.00 mol. %

Thus, the adopted model for the liquid line according to Eq. (5) satisfactorily agrees with the experimental results (Table 5) in the investigated temperature range of 270-360 K and can be used to calculate and construct the vapor line for the "dimethylzinc – dimethyl telluride" system.

The partial pressures of components in binary systems can be calculated based on the known dependence of the total saturated vapor pressure on the solution composition using the Duhem-Margules equation[5] in the form (9). The calculation of the "*Y-P*" vapor line was performed by obtaining a tabulated solution of the differential Eq. (9) by the Euler method, using the MS EXCEL spreadsheet processor.

$$\frac{dY}{dP} = \frac{Y(1-Y)}{P(x)(Y-x)} \qquad (9)$$

where Y is the content of dimethylzinc in the vapor composition with pressure P above the liquid containing $x = x_1$ (mole fractions) of dimethylzinc. Tabulation of the liquid line $P(x)$ was carried out with a step of $\Delta x = 0.01$[mol. %]. The initial value of the tabulation of the composition of the pair was $Y(x = 0) = 10^{-8} = 10^{-6}$ %. The initial change of dY_0 in the first step of the calculations was chosen to be minimal so as to ensure a positive value of dY in the calculations. At the same time, it was found that with temperature increasing the dY_0 value is increased according to the data in Table 11.

Table 11. Temperature dependence of the minimum initial change dY_0 in the first step of calculations to ensure a positive dY value in the process of vapor line calculations

T, K	dY_0, mol. %	T, K	dY_0, mol. %
270	0.01	320	0.6
280	0.01	330	0.7
290	0,3	340	0.9
300	0,3	350	1,1
310	0,4	360	1,3
305.0	10	309.3	10
309.7	10	352.2	1.1

For the vapor composition the dY value was calculated according to Eq. (10)

$$dY = \frac{Y(1-Y)}{P(x)(Y-x)} dP \qquad (10)$$

The **dP** value was calculated according to Eq. (11) as the product of the first derivative of the liquid line and the Δx value for the change in the liquid composition.

$$dP = \Delta P = \frac{dP(x)}{dx} \Delta x \qquad (11)$$

The tabulation of the first derivative for the liquid line was carried out according to Eq. (12), which was obtained by differentiating Eq. (5)

$$\frac{dP(x)}{dx} = LNx^{N-1} \qquad (12)$$

The vapor composition (Y) was tabulated according to Eqs. (13) and (14), where i is the row number in EXCEL spreadsheet for Y_i value.

$$Y_{i+1} = Y_i + \Delta Y_i \qquad (13)$$

$$\Delta Y_i = \frac{Y_i(1-Y_i)}{P(x_i)(Y_i - x_i)} \frac{dP(x_i)}{dx} \qquad (14)$$

Fig. 8 provides examples of the isothermal *P-X* diagrams of the state for the liquid and vapor lines at temperatures of 300 K, 270 K, and 360 K. These temperatures correspond to the points where the minimum (0.9 %) and maximum (28.1 % and 27.1 %) relative deviations of the experimental data from the model dependence, constructed according to Eq. (5), occur along the liquid line. The change in the position of the experimental points relative to the liquid line according to the model Eq. (5) is consistent with the change in the sign of the absolute deviations of the P_{LIMIT} experimental points (Table 10) from the calculated values.

A comparison was made for the calculated data for the vapor line with the experimental points obtained in the literature.[10] Experimental and calculated data for the steam line agree satisfactorily, which confirms the possibility of applying this technique to similar systems. Above in Table 10, there are deviations of the experimental points for P_{LIMIT} from the values calculated according to the model Eq. (5) for the liquid line. Figs. 9 and 10 show that these deviations for the temperatures at the moments of complete evaporation are consistent with the other temperatures that were chosen for the calculation with a temperature step of 10 degrees.

In the case of temperatures of complete evaporation (305.0; 309.7; 309.3; 352.2 K), the relative deviations for calculated values from experimental values are in ranges of 0.6-5.8 % and of 2.5-24.8 % for an equimolecular solution, and the content of dimethylzinc 70.32 mol. %, respectively. For the complete evaporation temperatures, the deviations of the experimental points for the vapor line from the calculated values (*ΔP, Pa*) are given in Table 12, from which it can be seen that the smallest relative deviations of 1.6 % and 2.1 % are observed for temperatures of 309.5 K and 352.2 K.

Fig. 9 shows the isothermal *P-X* diagrams of the state, for liquid and vapor lines at temperatures of complete evaporation (305.0; 309.7; 309.3; 352.2 K) for the equimolecular solution and for the solution with dimethylzinc content of 70.32 mol. %.
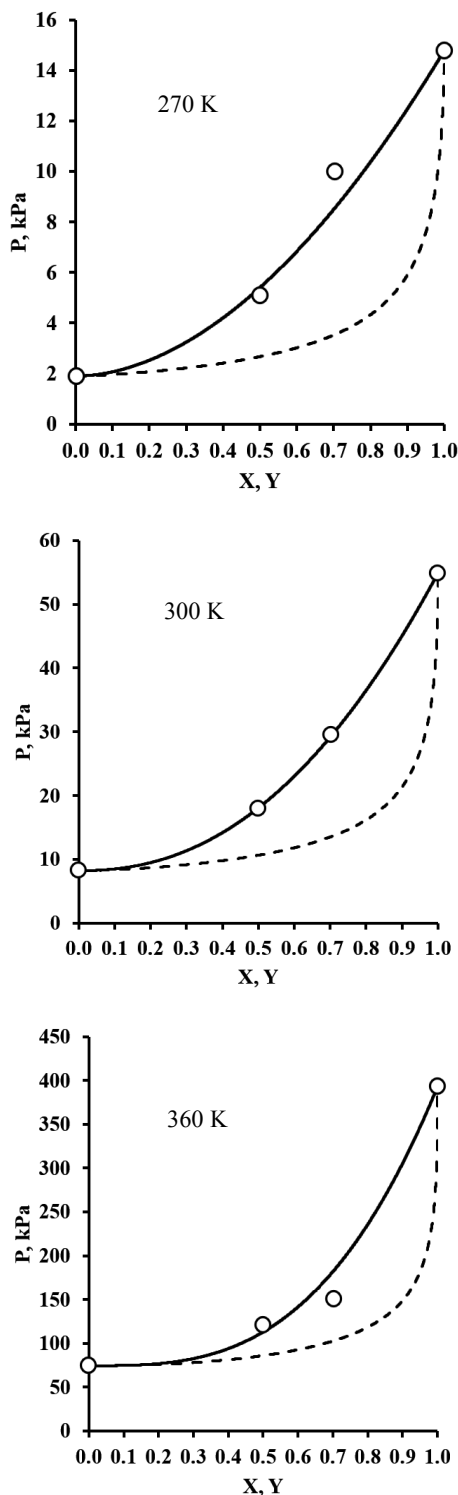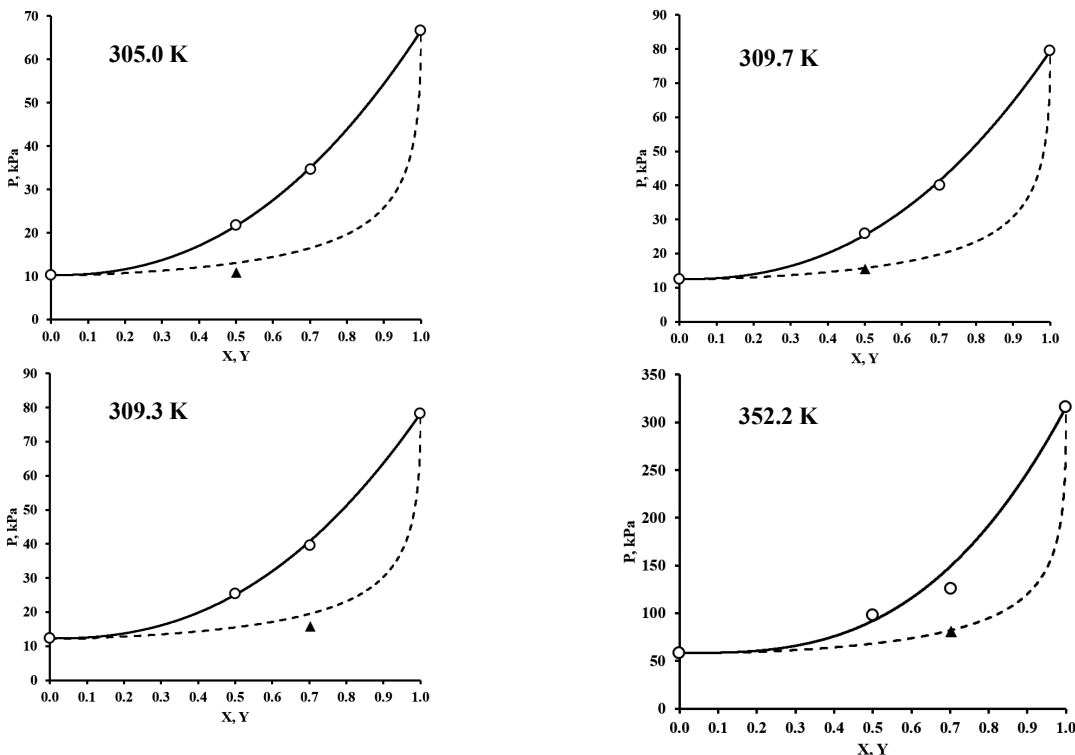

Fig. 8. Isothermal state diagrams of the vapor-liquid equilibrium for the dimethylzinc dimethyl telluride system. Lines of liquid (solid) and vapor (dashed) for temperatures 270 K, 300 K, 360 K and experimental points on the liquid line for the dimethylzinc content in the liquid of 70.32 mol. % and 50.00 mol. %

Table 12. Deviation of experimental points from calculated values for the vapor line at temperatures of complete evaporation

T, K	Content of Zn(CH$_3$)$_2$ in liquid, x_1	Calculated content of Zn(CH$_3$)$_2$ in vapor, Y_1	Calculated value of pressure, Pa for Y_1	Experimental value of pressure, Pa for Y_1	Deviation ΔP, Pa
305.0	0.5000	0.50002	13066	10787	2279
309.7	0.5000	0.50009	15751	15502	249
309.3	0.7032	0.70317	19551	15818	3733
352.2	0.7032	0.70316	82305	80584	1721

Fig. 9. Isothermal diagrams of the vapor-liquid equilibrium state for the dimethylzinc dimethyltelluride system. Calculated model liquid (solid) and vapor (dashed) lines for experimental temperatures of complete evaporation and experimental points on the liquid (circle) and vapor (triangle) lines for dimethylzinc content of 70.32 mol. % and 50.00 mol. % in liquid

Based on total vapor pressure (P) according to Eq. (15) the partial pressures (P_1, P_2) of the components are calculated for these temperatures.

$$P_1 = Y_1 P , \qquad (15)$$

For temperatures of 270 K, 300 K, and 360 K, Fig. 10 shows the dependence of the total vapor pressure and the partial pressures of the components on the composition of the solution. It can be seen (Fig. 10) that the content of dimethylzinc in the solution increases in the range of 22.325 %, 26.785 % and 33.677 % for the moment of equality of partial pressures with increasing temperature in the series of 270 K, 300 K and 360 K.

Also, according to Eq. (16), the separation coefficient (α) was calculated from the composition of the solution (x_1) (Fig. 11).

$$\alpha = \frac{x_2 Y_1}{x_1 Y_2} . \qquad (16)$$

The separation coefficient increases with increasing dimethylzinc content up to 82 mol. % and decreases with increasing temperature, but after that, the order with respect to the effect of temperature changes to the opposite, *i.e.*, a smaller partition coefficient is observed at lower temperatures.

The dependence of vapor composition (Y_1) on the solution composition (x_1), which is shown in Fig. 12, indicates that an increase in temperature from 270 K to 360 K worsens the components separation of the binary solution, especially in the area up to 10 mol. % of dimethylzinc.
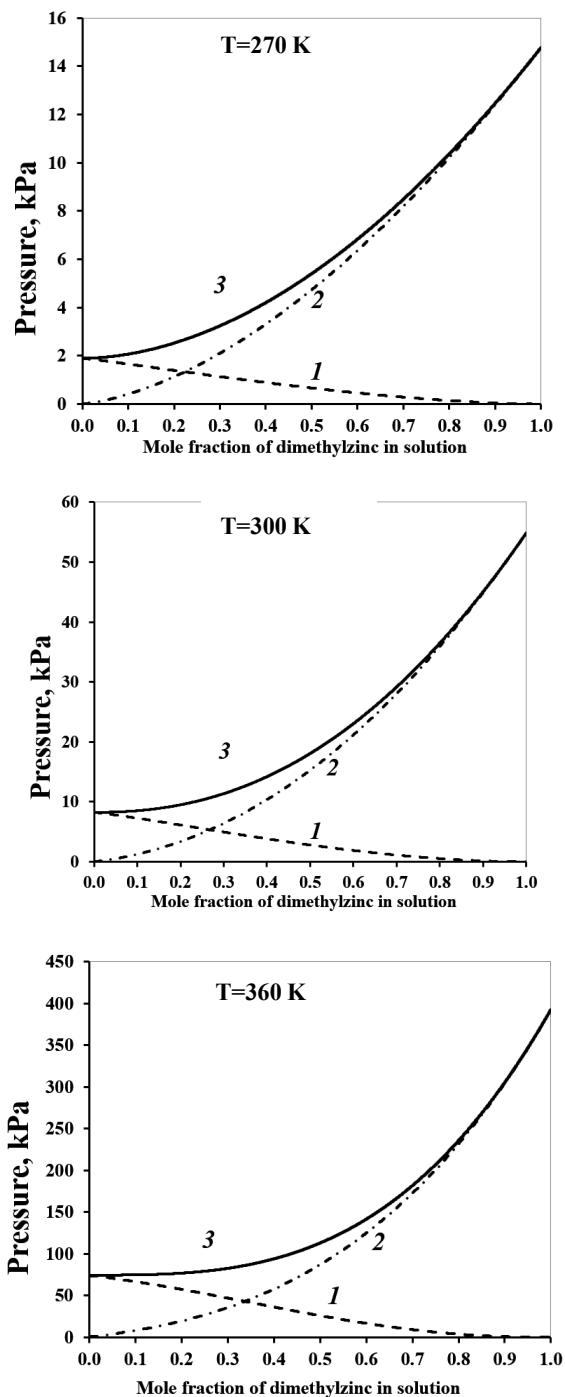
Fig. 11. Dependencies of the separation coefficient (α) on the content of dimethylzinc (x) in the binary solution at various temperatures

Fig. 12. Dependencies of the vapor phase composition (Y) on the content of dimethylzinc (x) in the binary solution of dimethylzinc-dimethyl telluride at various temperatures

Fig. 10. Dependencies of the components partial pressures (p_1, p_2) on the dimethylzinc content (x_1) in a binary solution $Zn(CH_3)_2$ and $Te(CH_3)_2$ at various temperatures: 1) $Te(CH_3)_2$; 2) $Zn(CH_3)_2$; 3) total pressure

4. Conclusions

Using the method, which is proposed in this work, for calculating isothermal diagrams of liquid – vapor equilibrium for the system dimethyl zinc – dimethyl telluride we obtained the results which show the adequacy of the model applied to a limited set of experimental data.
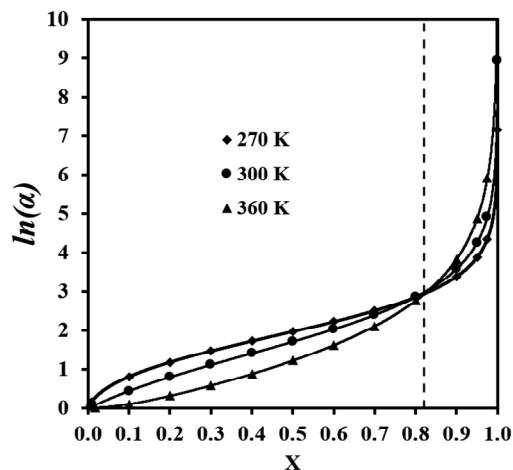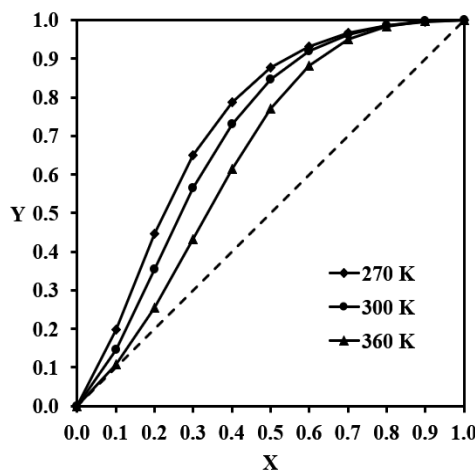
The temperature dependence of saturated vapor pressure for the dimethylzinc-dimethyltelluride system was experimentally determined in the temperature range of 270-360 K using the static method with a membrane zero-manometer. Utilizing the obtained temperature dependences of the saturated vapor pressure over dimethylzinc-dimethyltelluride solutions, with dimethylzinc contents of 50.0 mol. % and 70.32 mol. %, isothermal sections were constructed at temperatures of 280 K, 290 K, 300 K, 310 K, and 320 K.

Approximation was carried out for the calculated pressures at the indicated temperatures to the pressure corresponding to the evaporation of an infinitely large mass of this solution, the composition of which can be

considered constant. It was established that the dependence of the total vapor pressure on the dimethylzinc content (x_1 – mole fraction) at a certain temperature can be approximated by a power function $P = K + Lx_1^N$. The resulting equations were used to calculate the vapor composition as a numerical solution of the Duhem–Margules equation in a differential form. The partial pressures and distribution coefficient for the dimethylzinc – dimethyltelluride system were also calculated.

The proposed method, which rationally combines the use of the generalization of data between the solution mass and the pressure according to the inversely proportional semi-logarithmic dependence, of the power function for describing the liquid line and of the numerical solution for the differential form of the Duhem-Margules equation, for small samples of substances which composition changes in the process of evaporation, allows to determine the composition of the equilibrium phases to describe the "liquid-vapor" equilibrium in the absence of an azeotrope. The obtained data can be useful both for thermodynamic calculations of the "liquid-vapor" equilibrium and for calculating the processes of separation of binary systems using rectification.

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МЕТОД ОТРИМАННЯ ІЗОТЕРМІЧНИХ ДІАГРАМ РІВНОВАГИ РІДИНА–ПАРА СИСТЕМИ ДИМЕТИЛ ЦИНК–ДИМЕТИЛ ТЕЛУРИД

Анотація. *За отриманими експериментальними температурними залежностями тиску насиченої пари розчинів диметилцинк – диметилтелурид з вмістом диметилцинку 50,0 та 70,32 % (мольн.) зроблено ізотермічні перерізи (280, 290, 300, 310 та 320 К). На основі обмеженого набору експериментальних даних для рівноваги "рідина–пара" проведено розрахунок складу пари за рівнянням Дюгема – Маргулеса, а також парціальних тисків та коефіцієнту розподілу системи диметилцинк – диметилтелурид.*

Ключові слова: *діаграми стану, рівноваги рідина–пара, диметилцинк–диметилтелурид, тиск пари.*