P-V-T BEHAVIOR OF VAPOR MIXTURES

OF ALCOHOLS WITH WATER

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ABSTRACT

On the installation by method «piezometer of constant volume» the experiences on measurement of density and saturation pressure of vapors of «ethyl alcohol + water» mixtures were carried out at various range of pressure, temperature and concentration. The measurements were carried out on izochors for avoidance of issue of substance, as with high temperatures the mixtures having low temperatures of boiling, strongly evaporate during issue and it influences an error of measurement. An error of the experiments is calculated according to the recommendations of metrology of services and has made: for pressure - 0,05 %, for temperature - 0,002 K and density in single-phase area - 0,1 %, near to a saturation line - 0,2%. Behavior of thermal properties in various thermodynamic coordinates was analysed. The received material has allowed to make the equation of a condition in virial form and thus second and third virial coefficients are allocated. We obtained the virial coefficients by two independent methods, namely, graphically and analytically. The latter method allowed a step-by-step extension of the interval of densities on the isotherm with the inclusion of additional experimental points.

KEY WORDS: aliphatic alcohols, piezometer, pressure, temperature, virial coefficients,.

1. INTRODUCTION

Searching alternative radiants of a solar energy in various branches today is actually. At present moment in industrially developed countries low and highly potential solar installations is widely applied. A very small quantity of works is devoted to research P-V-T dependence of water mixtures of aliphatic alcohols. The P-V-T the dependencies are necessary for rational development, of designing heat- mass transfer of processes and equipment, choice optimum thermogydrodynamics modes. Study of water mixtures of alcohols also promote creation of molecular-kinetic theory of two and more components of mixtures. In view of this, the present work represents certain scientific and practical interest. For research of P-V-T of dependence the experimental installation on a method «piezometer of constant volume» is assembled.

2. MEASUREMENTS

We investigate thermal properties of a system consisting of water and ethyl alcohol. The experiments under the definition P-ρ-T dependence were carried out on experimental installation realizing a method «piezometer of constant volume» [1]. The volume of piezometer is $350{,}13\cdot10^{-6}$ m^3. For research the alcohols of the mark "CHD" and bi-distillate water were used. The mixtures have been prepared by a weight way on analytical balance. The measurements have carried out. At high temperatures mixtures having low temperatures of boiling, is force evaporate during an issue and it influences an error of a measurement. The experiments were carried out at an interval of density 5-50 kg/m^3. At reaching of the following temperature of a measurement with the help of thermocontroller VRT-2 the stabilization of temperature within 1-3 hours in an association from a value of temperature was observed. The measurements of temperature were carried out by two platinum thermometers of the mark PRT-10. The obtained values represent a full picture by a modification thermophysical properties in a steam condition. These values in such interval are obtained for the first time. Therefore we could not compare them to literary values. In the table 1 obtained P-ρ-T values of investigated vapors are shown. In the table 2 obtained P_s-ρ_s-T_s values of investigated vapors are shown. In the figures 1, 2 the P_s -T_s and ρ_s-T_s dependencies in various concentrations are shown.

3. ANALYSIS

The obtained values are circumscribed with the equation of a state in the virial form:

$$z = 1 + B\rho + C\rho^2 + ... \qquad (1)$$

Where: B and C - accordingly, second, third and etc. virial coefficients. The virial coefficients are shown in Table 3. Calculation of virial coefficients produced by two independent methods - graphical, offered in [2] and analytical method [3], offering series expansion of an interval of density on an isotherm with inclusion addition experimental points. The graphic method of the definition of virial coefficients has supplemented and has confirmed a validity of application of analytical method. The virial coefficients are shown in Table 3. In the figure 3 dependence of second virial coefficient from concentration are shown. The virial coefficients B and C dependence from temperature and concentration in following form:

$$B = \sum_{i=0}^{3} T^i \sum_{j=0}^{3} b_{ij} X^j; \qquad C = \sum_{i=0}^{3} T^i \sum_{j=0}^{3} c_{ij} X^j; \qquad (2)$$

In the table 4 the value of coefficients b_{ij} and c_{ij} in the equation (2) are shown. The P_s-ρ_s-T_s values of investigated vapors are calculated with the following equation:

$$P_s = \sum_{i=0}^{4} T^i \sum_{j=0}^{4} d_{ij} X^j; \qquad \rho_s = \sum_{i=0}^{4} T^i \sum_{j=0}^{4} e_{ij} X^j; \tag{3}$$

The values of b_{ij} and c_{ij} coefficients in equation (3) are shown in Table 5.

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Table 1. P-ρ-T values of investigated «ethyl alcohol+ water» vapor mixtures

X=0,25 %					
P, MPa	**ρ, kg/m^3**	**P, MPa**	**ρ, kg/m^3**	**P, MPa**	**ρ, kg/m^3**
T=373,15K		**T=473,15K**		3,594	54,3999
0,1	0,95	0,1	0,6133	**T=523,15K**	
0,174	3,04	0,2	1,2396	0,1	0,5528
T=398,15K		0,5	3,1881	0,2	1,1071
0,1	0,7609	1,0	6,8174	0,5	2,7972
0,2	1,6764	1,5	11,4246	1,0	5,7072
0,362	5,97	2,0	19,3	1,5	8,7971
T=423,15K		2,251	32,5	2,0	12,1686
0,1	0,6998	**T=498,15K**		2,5	16,0785
0,2	1,4425	0,1	0,5813	3,0	20,2365
0,5	4,12	0,2	1,1697	3,5	25,3753
0,669	10,8	0,5	2,9631	4,0	32,0125
T=448,15K		1,0	6,0752	4,5	40,9766
0,1	0,6541	1,5	9,5112	5,0	54,8071
0,2	1,3338	2,0	13,4785	5,5	86,6000
0,5	3,57	2,5	18,7883	5,66	111,6001
1,0	9,2	3,0	25,5		
1,246	17,7	3,5	44,9		

Continue of Table 1

X=0,50 %					
P, MPa	**ρ, kg/m^3**	**P, MPa**	**ρ, kg/m^3**	**P, MPa**	**ρ, kg/m^3**
T=373,15K		**T=473,15K**		4,0	63,9
0,1	1,0479	0,1	0,7409	4,253	80,5001
0,174	5,1	0,2	1,4923	**T=523,15K**	
T=398,15K		0,5	3,8156	0,1	0,6673
0,1	0,9173	1,0	8,02	0,2	1,348
0,2	2,0001	1,5	13,6	0,5	3,3537
0,451	9,4	2,0	21,3	1,0	6,7791
T=423,15K		2,5	40,02	1,5	10,3027
0,1	0,8472	2,574	44,8	2,0	13,9774
0,2	1,7632	**T=498,15K**		2,5	17,8842
0,5	5,2556	0,1	0,7016	3,0	22,0283
0,829	16,9	0,2	1,4043	3,5	26,7301
T=448,15K		0,5	3,5687	4,0	32,0156
0,1	0,7878	1,0	7,3111	4,5	38,2198
0,2	1,6014	1,5	11,4	5,0	45,981
0,5	4,2858	2,0	16,03	5,5	56,1
1,0	10,5034	2,5	21,6	6,0	74,0
1,500	24,7	3,0	29,0131	6,5	102,4999
1,523	26,7	3,5	41,1182	6,76	144,1999

Continue of Table 1

X=0,75 %					
T=373,15K		1,523	30,1	4,0	62,4
0,1	1,3969	**T=473,15K**		4,413	93,4001
0,14	2,4799	0,1	0,9773	**T=523,15K**	
0,207	5,97	0,2	1,9725	0,1	0,8786
T=398,15K		0,5	5,06	0,2	1,7589
0,1	1,2128	1,0	10,5494	0,5	4,4195
0,2	2,5746	1,5	17,1693	1,0	8,9291
0,484	11,02	2,0	25,446	1,5	13,5453
T=423,15K		2,5	39,0295	2,0	18,3823
0,1	1,1199	2,723	50,3	2,5	23,4448
0,2	2,2967	**T=498,15K**		3,0	28,9066
0,5	6,4389	0,1	0,9245	3,5	34,8543
0,8	13,1003	0,2	1,8528	4,0	41,4285
0,921	19,4	0,5	4,6838	4,5	48,9547
T=448,15K		1,0	9,5721	5,0	57,8386
0,1	1,0423	1,5	14,8204	5,5	68,5026
0,2	2,117	2,0	20,5544	6,0	83,2437
0,5	5,569	2,5	27,0835	6,5	105,2
1,0	12,6837	3,0	35,1465	7,0	140,03
1,500	24,3	3,5	45,5861	7,191	163,8999

X - concentration of ethyl alcohol

Table 2. Experimental P_s-ρ_s-T_s values of vapors of «ethyl alcohol-water» mixtures

T, K	**P_s, Mpa**			**ρ_s, kg/m^3**		
	X=25%	**X=50%**	**X=75%**	**X=25%**	**X=50%**	**X=75%**
373,15	0,137	0,174	0,207	3,04	5,1	5,97
398,15	0,362	0,451	0,484	5,97	9,4	11,02
423,15	0,669	0,829	0,921	10,8	16,9	19,4
448,15	1,246	1,523	1,662	17,7	26,7	30,1
473,15	2,251	2,574	2,723	29,4	44,8	50,3
498,15	3,594	4,23	4,413	54,4	80,5	93,4
523,15	5,66	6,76	7,191	111,6	144,2	163,9

X - concentration of ethyl alcohol

Table 3. The virial coefficients of vapors of «ethyl alcohol- water» mixtures

T, K	$B \cdot 10^{-3}$, ì^3/kg			$C \cdot 10^{6}$, ì^6/kg^2		
	x=25%	x=50%	x=75%	x=25%	x=50%	x=75%
373,15	-0,185465	-0,1653	-0,1025516	-0,009429	-0,007525	0,00023
398,15	-0,0682	-0,065	-0,0449	-0,005406	-0,0009291	-0,000404
423,15	-0,039	-0,0360825	-0,0263047	-0,001846	-0,00031213	0,0000748
448,15	-0,024062	-0,021	-0,0159942	-0,0005032	-0,00013506	0,00005
473,15	-0,011411	-0,0092	-0,00818046	-0,00027795	-0,0001266	-0.000032
498,15	-0,0070732	-0,005318	-0,00409037	-0,0001199	-0,00006148	-0,000033
523,15	-0,0060012	-0,00381887	-0,00246604	-0,0000298	-0,00001826	-0,000015

Table 4. The values of b_{ij} and c_{ij} coefficients in equation (2).

b_{ij}		c_{ij}	
b_{00}=0,07381765631	b_{20}=-0,38323767·10^{-6}	c_{00}=0,073689695728	c_{20}=0,1079179150184·10^{-5}
b_{01}=1,23109152445	b_{21}=0,16610544·10^{-4}	c_{01}=-0,07140073424	c_{21}=-0,919878215317·10^{-6}
b_{02}=-0,0233493498	b_{22}=-0,31617397·10^{-6}	c_{02}=0,001520589533	c_{22}=0,1925418245556·10^{-7}
b_{03}=0,110494·10^{-3}	b_{23}=0,15021901·10^{-8}	c_{03}=-0,0000083115	c_{23}=-0,1039261741814·10^{-9}
b_{10}=-0,5647391·10^{-4}	b_{30}=0,484643·10^{-9}	c_{10}=-0,4887568·10^{-3}	c_{30}=-0,7920940932536·10^{-9}
b_{11}=-0,0078414605	b_{31}=-0,11700583·10^{-7}	c_{11}=0,44394172·10^{-3}	c_{31}=0,6350087874893·10^{-9}
b_{12}=0,149012·10^{-3}	b_{32}=0,22300821·10^{-9}	c_{12}=-0,9370852·10^{-5}	c_{32}=-0,13186739412·10^{-10}
b_{13}=-0,7067075·10^{-6}	b_{33}=-0,1061032·10^{-11}	c_{13}=0,50889658·10^{-7}	c_{33}=0,7077488692921·10^{-13}

Table 5. The values of d_{ij} and e_{ij} coefficients in equation (3).

d_{ij}		e_{ij}	
d_{00}=1489.826222023	d_{23}=-0.650494545115·10^{-5}	e_{00}=289.9105736876083	e_{23}=0.2433626993656·10^{-4}
d_{01}=-341.3186318606	d_{24}=0.2987440967467·10^{-7}	e_{01}=2270.54881624819	e_{24}=-0.7024045029294·10^{-7}
d_{02}=14.5282299368055	d_{30}=-0.711394330871·10^{-4}	e_{02}=-73.47549234994565	e_{30}=-0.2033572279958·10^{-4}
d_{03}=-0.2074722639609	d_{31}=0.1587540883061·10^{-4}	e_{03}=0.7512976033346068	e_{31}=-0.1158978257694·10^{-3}
d_{04}=0.94994060995·10^{-3}	d_{32}=-0.683851639907·10^{-6}	e_{04}=-0.00216937540039	e_{32}=0.3677927383029·10^{-5}
d_{10}=-13.7036242072156	d_{33}=0.9837698922783·10^{-8}	e_{10}=-2.952939122344314	e_{33}=-0.375110653986·10^{-7}
d_{11}=3.1097513288995	d_{34}=-0.45255442132·10^{-10}	e_{11}=-21.27769327869018	e_{34}=0.1082451034384·10^{-9}
d_{12}=-0.13287601786392	d_{40}=0.4016574839212·10^{-7}	e_{12}=0.6845441761278841	e_{40}=0.1393054781706·10^{-7}
d_{13}=0.00190193237	d_{41}=-0.889689946363·10^{-8}	e_{13}=-0.006994226172418	e_{41}=0.6742520851355·10^{-7}
d_{14}=-0.8721070336·10^{-5}	d_{42}=0.3848465720384·10^{-9}	e_{14}=0.201904266299·10^{-4}	e_{42}=-0.2121670006033·10^{-8}
d_{20}=0.0469782754214	d_{43}=-0.55512195775·10^{-11}	e_{20}=0.011484335009126	e_{43}=0.2161081767033·10^{-10}
d_{21}=-0.01056763008567	d_{44}=0.255813403172·10^{-13}	e_{21}=0.0745751491642582	e_{44}=-0.62343059599·10^{-13}
d_{22}=0.45334856547·10^{-3}		e_{22}=-0.002383825065231	

Figure 1. P_s-T_s dependencies of investigated mixtures in various concentrations.

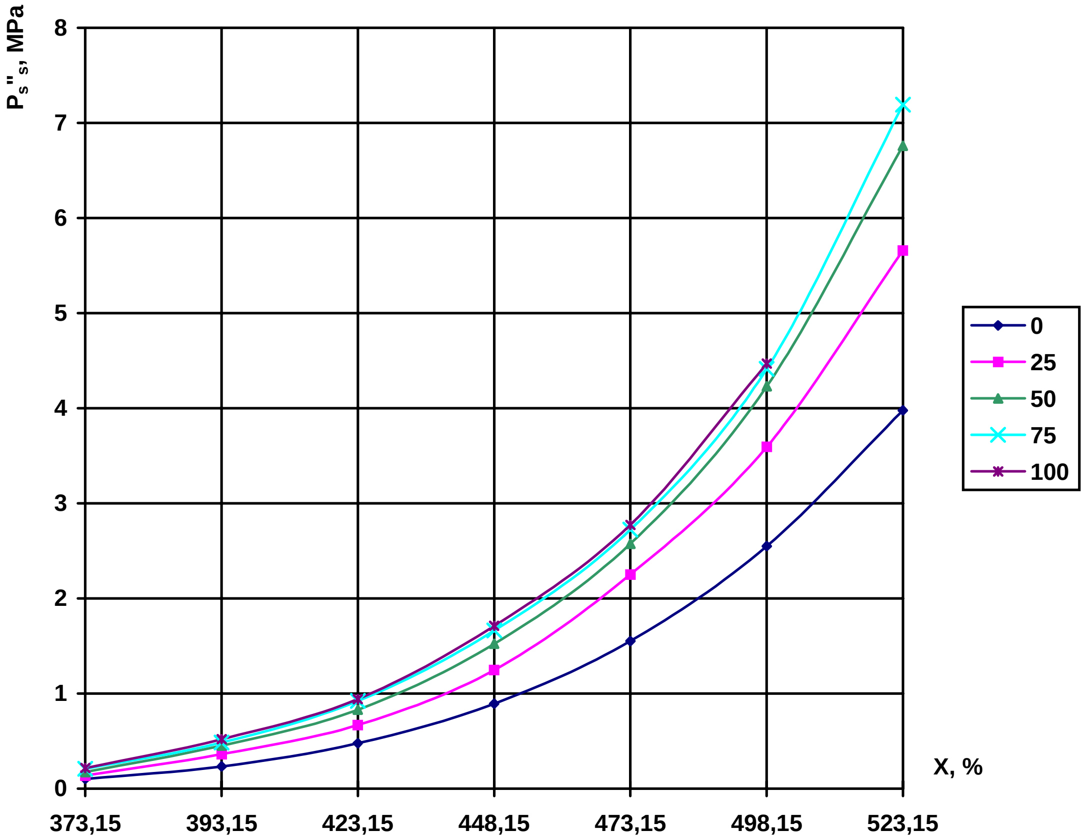

Figure 2. ρ_s-T_s dependencies of investigated mixtures in various concentrations.

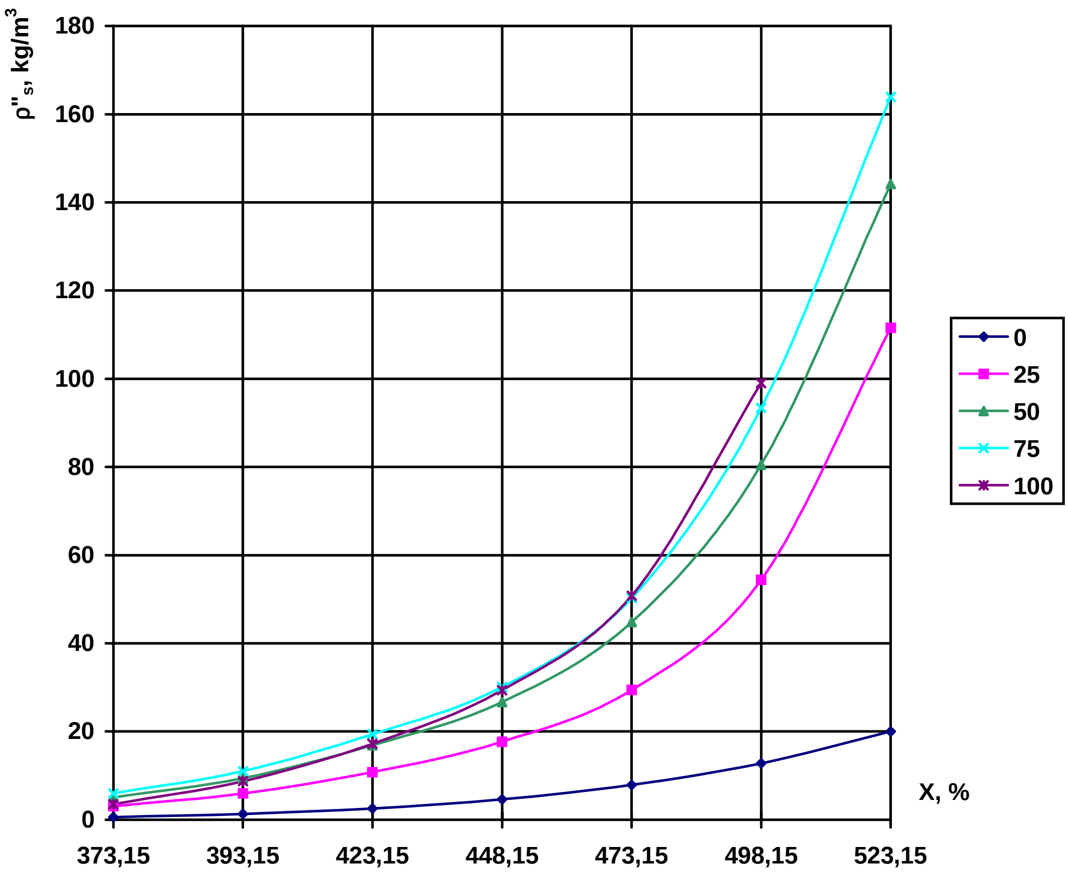

Figure 3. Dependence of second virial coefficient B from concentration of mixtures.