THE EXPERIMENTAL INVESTIGATION OF *P-ρ-T* DEPENDENCE OF METHANOL-WATER SOLUTIONS IN THE TEMPERATURE INTERVALS FROM –30°C TILL 30°C AND PRESSURE 1-200 BAR

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The experimental investigation of *P-ρ-T* dependence of the three binary solutions methanol-water with the molar compositions 75-25%, 50-50% and 25-75% in the temperature intervals from –30°C till 30°C and the pressure 1-200 bar. For the density measurement the good treated technique of the piezometer of the constant volume was used. The error of the obtained data doesn't exceed +-0,1%.

For the carrying out of experimental investigation of *P-ρ-T* dependence of methanol-water solution the experimental installation, earlier created by us, working by the method of the piezometer of the constant volume, was used [1]. The main element of the installation is thick-walled piezometer of the spherical form from the stainless steel 1X18H9T, which has the external diameter 140 mm, internal diameter 62 mm and volume ~123 cm^3 at t=20°C and P=1 bar. The two thin capillaries from the same stainless steel by the internal diameter 0,4 mm and wall thickness 0,8 mm are soldered in the lower connecting pipe of piezometer. With the help of the central capillary, the piezometer connects with fixing device and the system of the creation and measurement of the pressure, and the second capillary is used for the filling of the piezometer by the liquid and output of the last.

The use of the capillaries of the small diameter (0,4 mm) and the gate of the special construction allows us to lead the ballast volume to the very small value (0,2 cm^3), which is near 0,15% from the total piezometer volume, moreover, the capillary volume, situated in the band of the transitional temperatures (from thermostat temperature till room one) is equal 0,06 cm^3, i.e. 0.04% from piezometer volume.

All installation nodes, with which the investigated liquid and mercury connect, are produced from the stainless steel 1X18H9T. The choice of this steel is caused by its high anticorrosive properties. Moreover, nowadays its physical properties have been investigated in detail that allows us to calculate the corrections on piezometer deformation with exactness in the dependence on the temperature and pressure.

The piezometer thermostating is carried out in the liquid thermostat, supplied by the axial pump, providing the intensive circulation of the thermostating liquid on the contour, created by the small cylinder, where the pump is situated, by the big cylinder, where the piezometer is situated and the corresponding jet. For the improvement of the thermostating the liquid is given through the lower jet from the small cylinder to the big one tangentially. The intensive motion of the liquid provides the homogeneous temperature field on all thermostat volume and moreover, the regulation of the thermostat temperature and piezometer, consequently, with the investigated substance is carried out on the control for the temperature in the one point of the thermostat. The well heat transfer from the liquid to the piezometer accelerates the transition process from the one measurement mode to another one.

For the obtaining and maintenance of needed temperatures in tests constantly we pass the water from ultratermostat through copper coil, being in thermostat at t=15°C. The vapour of liquid nitrogen, the expenditure of which was regulated thinly with the help of vacuum pump and needle valves of special constructions, were passed through coil at t<15°C.

The pressure in the installation was created by the nitrogen supply into the autoclave and oil multiplier. The pressure though the mercury was passed to the investigated liquid. For the creation of the more high pressure the press of the deadweight ianometer MP-600 was used. Pressing by the press the nitrogen, situating in the oil multiplier and under the mercury in the autoclave, the pressure in the system with the initial pressure 80-100 bar can be reduce till 1000 bar.

In this paper the main attention is given to the assurance of high measurement accuracy of the experimental values: temperature, pressure and specific volumes (density).

For the measurement of the temperature two platinum thermometers of the resistance were used. One of them is exemplary one with coefficient $\frac{R_{100}}{R_0} = 1.39259$ and R_0=9.9980 Om of VNIIFTRI construction and another (long) thermometer is produced also in VNIIFTRI taking under the consideration the demands to the exemplary resistance thermometers. The sensitive element of the second thermometer is carried out from the plane of PL-1 type with coefficient $\frac{R_{100}}{R_0} = 1.39245$ and has the resistance R_0=10.9251 Om.

The reading of both resistance thermometers coincided to 0.01°C, that's why in experiments only one thermometer was used often, and another one was used for the periodic control of the stability of thermometers in time.

The excess pressures in the installation were measured by the deadweight ianometer MP-600 (class 0,01) and MP-60 (class 0,05). The total maximal error of the pressure measurement practically corresponds to the class of the exactness of the piston manometer.

It is need to note, that before the main experiment the special experiments on the pressure measurement of the saturated vapour of the simple water in the temperature interval from 200°C till critic one, were carried out on the installation. The obtained data are compared with the given ones of International constructional table [2]. The divergence on the pressure in all investigated temperature interval doesn't exceed ±0.,02 bar that proves good agreement degree of the above mentioned measurement accuracy of the temperature and pressure.

The specific volume of the investigated liquid is defined as partial from the division of piezometer volume of the investigated liquid, filling the piezometer at the measured temperature and pressure.

By analysis, of the measurement error of the main experimental values – temperatures, pressures, piezometer volume and mass of the investigated substance, it is established, that maximal sum relative fault of the density definition is equal ≈±0,05-0,10%, which has been proved in the previous experiments with the simple water and toluol.

After checking experiments, the density investigations of binary solutions methanol-water in the temperature interval from –30°C till 30°C and pressures from 1,0 till 200 bar had been begun. Toward this end three two-component solutions methanol-water with molar compound:75-25%, 50-50% and 25-75% had been prepared. The solutions were prepared by the weighing ADB-200 on the analytical scales with the error ±0,01% on mol. Moreover, the methanol by "ch.d.a." type was used, which repeatedly was treated detail purification and the distillated water.

Table 1. Density values of methanol-water solution of 25-75% molar composition

P, bar	ρ, $\frac{kg}{m^3}$	P, bar	ρ, $\frac{kg}{m^3}$	P, bar	ρ, $\frac{kg}{m^3}$	P, bar	ρ, $\frac{kg}{m^3}$	P, bar	ρ, $\frac{kg}{m^3}$	P, bar	ρ, $\frac{kg}{m^3}$	P, bar	ρ, $\frac{kg}{m^3}$
t=-30°C		t = -20°C		t = -10°C		t = 0°C		t=10°C		t - 20°C		t = 30°C	
4,025	965,51	5,107	961,01	2,173	955,50	1,348	950,89	3,245	946,01	6,112	941,52	1,007	936,50
19,153	966,50	22,543	961,52	15,995	956,50	22,349	952,01	19,091	946,89	14,146	941,89	21,094	937,44
50,005	968,01	48,891	962,85	53,763	958,53	57,009	953,81	55,122	948,75	49,217	943,50	57,199	939,41
79,149	969,52	83,504	964,63	89,750	960,51	77,943	954,89	80,245	950,02	79,014	945,18	84,990	940,55
120,845	971,25	130,941	967,52	128,546	962,52	115,240	956,562	118,907	952,01	117,394	947,00	119,044	942,45
157,213	973,52	155,848	968,62	162,005	963,72	160,017	959,01	158,799	954,01	157,205	949,01	161,217	944,33

Table 2. Density values of methanol-water solution of 50-50% molar composition

P, bar	ρ, $\frac{kg}{m^3}$	P, bar	ρ, $\frac{kg}{m^3}$	P, bar	ρ, $\frac{kg}{m^3}$	P, bar	ρ, $\frac{kg}{m^3}$	P, bar	ρ, $\frac{kg}{m^3}$	P, bar	ρ, $\frac{kg}{m^3}$	P, bar	ρ, $\frac{kg}{m^3}$
t = -30°C		t = -20°C		t = -10°C		t = 0°C		t=10°C		t = 20°C		t = 30°C	
3,125	925,21	2,115	917,62	1,653	910,04	2,145	902,71	1,128	895,08	3,005	887,73	2,065	880,21
17,413	926,03	16,525	918,41	13,343	910,50	15,123	903,35	18,175	895,82	13,245	888,21	19,153	881,24
53,248	927,50	56,253	980,25	51,245	912,53	53,158	905,27	50,245	897,55	52,125	890,45	48,058	882,72
85,198	929,02	79,135	921,31	81,375	913,89	118,128	908,61	76,343	899,01	77,605	891,70	80,035	884,63
122,051	930,75	123,075	923,51	119,023	915,84	161,062	910,65	124,050	901,52	123,041	894,16	125,148	887,15
160,130	932,50	159,980	925,10	150,085	917,88			159,990	903,33	160,015	896,11	159,980	888,79

Table 3. Density values of methanol-water solution of 75-25% molar composition

P, bar	ρ $\frac{kg}{m^3}$	P, bar	ρ, $\frac{kg}{m^3}$	P, bar	ρ, $\frac{kg}{m^3}$	P, bar	ρ, $\frac{kg}{m^3}$	P, bar	ρ, $\frac{kg}{m^3}$	P, bar	ρ, $\frac{kg}{m^3}$	P, bar	ρ, $\frac{kg}{m^3}$
t = -30°C		t = -20°C		t = -10°C		t = 0°C		t = 10°C		t = 20°C		t = 30°C	
1,941	882,54	3,007	873,15	4,543	864,52	2,322	855,51	2,778	847,03	1,004	838,02	6,192	829,75
17,427	883,21	23,483	874,44	19,817	865,53	22,841	857,02	25,993	848,51	19,752	839,49	23,714	831,11
37,546	884,15	49,527	876,00	45,713	867,36	54,724	859,24	55,778	850,52	43,845	841,23	47,512	832,66
79,841	886,12	85,841	878,03	75,841	869,12	81,941	860,76	94,507	853,04	88,392	844,44	81,341	835,31
118,241	888,10	120,712	880,01	112,541	871,13	130,330	863,53	133,118	885,47	140,211	847,50	124,214	838,00
157,844	890,11	161,214	882,02	158,347	873,66	159,971	865,40	161,079	857,28	160,785	849,01	159,973	840,75

The density measurements of each from the mentioned binary solutions were carried out on five quasi-isochore. On each quasi-isochore the measures were carried out with step 10°C and 7 pressure values and densities had been obtained. In sum 126 experimental values of densities, which are given in the tables 1,2 and 3 were obtained. The internal agreement of the obtained data was checked by the construction of the different isothermal and isobaric cross sections. The divergence of the experimental points relatively smoothing curves doesn't exceed ±0,01%.

Moreover, the density dependences from the compound fig.1 and 2 had been constructed and then the data were used for pure water and methanol [2,3]. As it is seen from these figures the solution density methanol-water doesn't obey the simple additivity law, and it is inclined to the side of the density decrease. The maximal inclination corresponds to molar compound ~50-50% and is equal 4,6 and 5,0% at the positive temperatures. With the temperature decrease this inclination decreases and changes the sign.

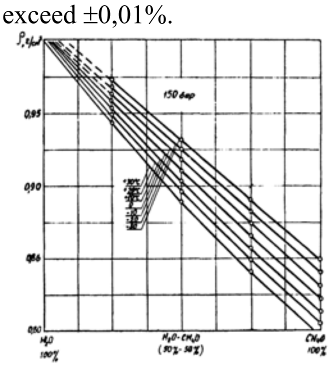

Fig.1. The dependence of the density of the binary solutions methanol-water on the concentration at *P*=50 bar.

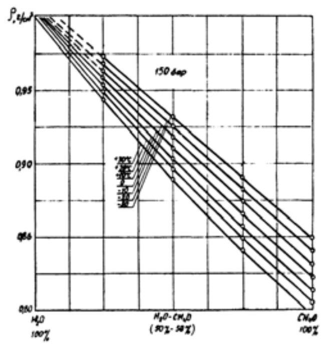

Fig.2. The dependence of the density of binary solutions methanol-water on concentration at *P*=150 bar.

Such data for the given solution is absent in literature and have been obtained firstly at the given temperatures.

Conclusions

The measurements of *P-ρ-T* dependence of binary solutions of methanol-water with molar compounds75-25%б 50-50% and 25-75% in the temperature intervals from –30°C till 30°C and pressures 1-200 bar were carried out on the experimental installation, working on the method of piezometer of the constant volume. In installation construction and technique of the measure carrying out the corresponding changes, taking under consideration the specific properties of the investigated substance and material and temperature region had been included. Firstly, the *P-ρ-T* dependences of three binary solutions methanol-water were measured on the given installation and the new density values had been obtained. The maximal relative error of the experimental data doesn't exceed ±0,01%.

The graph analytical treatment is established, that in the investigated temperature and density interval, the density of solution methanol-water doesn't obey simple additivity law, and is inclined to the side of the density decrease. The maximal inclination corresponds to molar compound 50-50% and is equal 4,6 and 5,0% at positive temperatures. With the temperature decrease this inclination decreases and changes the sign.

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METANOL – SU QARIŞIĞI R-ρ-T ASILILIĞININ –30⁰S–DƏN 30⁰S–YƏDƏK TEMPERATUR VƏ 1-200 BAR TƏZYİQ İNTERVALINDA TƏCRÜBİ TƏDQİQİ

30^0S-dən do 30^0S –yədək temperatur və 1-200 bar təzyiq intervalında 75-25%, 50-50% və 25-75% mol tərkibli üç binar metanol-su qarışığının R-ρ-T asılılığı təcrübi tədqiq olunmuşdur. Ölçülər yüksək dərəcədə təkmilləşdirilmiş sabit həcmli pyezometr üsulu ilə yerinə yetirilmişdir. Alınan nəticələrin nisbi xətası ±0,1%-dən çox deyil.

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ЭКСПЕРИМЕНТАЛЬНОЕ ИССЛЕДОВАНИЕ Р-ρ-Т ЗАВИСИМОСТИ РАСТВОРОВ МЕТАНОЛ-ВОДА В ПРЕДЕЛАХ ТЕМПЕРАТУР ОТ -30^0С ДО 30^0С И ДАВЛЕНИЙ 1-200 БАР

Проведено экспериментальное исследование Р-ρ-Т зависимости трех бинарных растворов метанол-вода с мольными составами 75-25%, 50-50% и 25-75% в пределах температур от -30^0С до 30^0С и давлений 1-200 бар. Для измерения плотности использована хорошо отработанная методика пьезометра постоянного объема. Погрешность полученных данных не превышает ±0,1%.

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