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EEXPERIMENTAL STUDY OF P, V, T DEPENDENCE AND EQUATION OF STATE OF β CYANOPROPIONALDEHYDE

Abstract

The density of β-cyanopropionaldehyde, in a wide range of temperature and pressure was determined. Also, the heat capacity of that aldehyde at constant pressure and different temperatures was experimentally measured. The research has been cleared by different formulas.

Keywords: *cyanpropion, aldehyde, temperature, density, pressure*

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β - sianprapion aldehidinin təcrübi tədqiqi və hal tənliyi

Xülasə

β-sianprapion aldehidinin geniş temperatur və təzyiq intervalında sıxlığı təyin edilmiş və ümumiləşmiş hal tənliyi yazılmışdır. Həmçinin, aldehidin sabit təzyiqdə və müxtəlif temperaturda istilik tutumu eksperimental olaraq ölçüldü. Tədqiqat müxtəlif düsturlarla izah olunub.

Açar sözlər: *sianprapion, aldehid, temperatur, sıxlıq, təzyiq*

Introduction

We use for research samples of β - cyanopropionic aldehyde, manufactured at the Novocherkassk Chemical Plant, chemical reagents of the grades KhCh (chemically pure), ChDA (pure for analysis), OCH (special pure).

The passports of these substances indicated the values of the normal boiling point in density at a temperature of 293℃.

The β-cyanopropionic aldehydes under study were preliminarily purified by distillation under vacuum.

In this case, we were guided by the methodological instructions for the purification of oxygen-containing compounds given in (Anisimov, Kovalchuk, 1978; Anisimov, Ovodova, 1971: 1092). The degree of purity was controlled by chromatographic analysis using Tsvet-4 and Pai

chromatographs. Purity control carried out by us using various methods showed that the content of the main substance for β-cyanopropyldehyde is 99.91%.

Measurements of the density of β-cyanopropionic aldehyde were carried out using isotherms.

The densities of β-cyanopropionic aldehyde were studied in the pressure range of 0.1-58.9 MPa at a temperature of 290-505 K.

Experimental data on the density of β-cyanopropionic aldehyde in a wide range of state parameters using the hydrostatic weighing method (Chashkin, 1971: 29-33; Mutalibov, Shubin, Makhmudov, 1975: 62-65) are presented in Table. 1.

Measurements of the density of β-cyanopropionaldehyde were carried out. On 16 isotherms (280; 290.4; 300.1; 320.1; 333.7; 340.1; 360; 370; 372.3; 404.9; 427.8; 463.0; 505.0 K) 131 experimental values were obtained.

β-cyanopropionic aldehyde is widely used in the technology of producing glutamic acid and thrintophene, which are technologically important substances for many industries.

Experimental data on the density of β-cyanopropionaldehyde.

(ρ, Kq/m^3) **Table 1.**

P,M	0,1	5,0	9,9	19,7	29,5	39,3	49,1	58,9
220,0	1054,1	1056	1058,0	1061,8	1065,5	1069,1	1072,6	1073,0
240,0	1040,4	1042,6	1044,8	1049,1	1053,1	1057,3	1061,2	1064,2
260,0	1025,3	1027,8	1030,3	1035,1	1039,7	1044,2	1048,5	1052,5
280,0	1008,9	1011,7	1014,5	1019,9	1025,1	1030,0	1031,8	1032,4
290,4	999,9	1002,8	1006,0	1010,5	1016,5	1022,2	1026,8	1031,4
300,1	991,5	994,7	997,8	1003,8	1009,6	1015,1	1020,3	1024,6
314,9	977,3	980,8	924,2	990,3	996,9	1003,8	1008,0	1013,5
320,1	973,5	977,1	980,6	987,3	993,7	999,7	1005,4	1007,4
333,7	960,7	964,0	967,3	974,9	981,8	988,4	993,7	999,4
380,1	-	958,9	962,9	970,3	977,3	983,9	990,1	996,7
360	-	940,7	945,7	953,3	960,9	968,1	974,8	976,1
372,3	-	928,8	933,6	941,4	850,3	957,7	954,5	970,9
404,9	-	898,4	904,3	913,7	923,5	981,5	989,5	946,8
427,8	-	877,6	834,0	894,2	905,4	913,8	922,6	930,0
463,0	-	841,7	848,5	861,1	874,4	884,7	894,1	903,0
505,0	-	795,5	805,1	822,0	836,8	849,5	860,0	870,5

The availability of sufficiently reliable P, V, T data for individual liquids and their mixtures allows us to draw up an experimentally substantiated equation of state for them. Empirical equations of state should perhaps have a simpler form and should describe the experimental data so accurately that with their help it is possible to obtain sufficiently reliable data not only on the thermal, but also on the caloric properties of the systems under study.

Currently, to describe the thermodynamic properties of liquids, the equation of state in the form is widely and very successfully used (Guesinov, 1978; Polyak, 2009):

$$P = \frac{A(T)}{V^n} + \frac{B(T)}{V^m}$$

where P is pressure, V is specific volume, A(T) and B(T) are temperature functions, n and m are positive integers.

Our analysis showed that for the systems we studied, the equation of state will have the following form:

$$P = \frac{A(T)}{v^2} + \frac{B(T)}{v^8} \qquad (2)$$

where

$$A(T) = \sum_{i=0}^{3} a_i \left(\frac{T}{100}\right)^i; \quad B(T) = \sum_{i=0}^{3} b \left(\frac{T}{100}\right)^i_i \qquad (3)$$

The exponents *n* and *m* are determined on the condition that in *v* coordinates $Pv^n - \frac{1}{v^{m-n}}$ the isotherms are straight. For the substances we studied, the values n=2 and values m=8 were found by trial and error.

On a computer, using the experimental least squares method of the density of individual substances, it is possible to determine the values of the coefficients ai and bi in the equation of state (2). The calculations and comparisons performed show that the equation of state with the given coefficients approximates the experimental data with deviations close to the estimated measurement error. Maximum deviations lie in the range of 0.10 - 0.2% (Mustafaev, Ganiev, 1981; Ganiyev, Abbasov, 2010).

The sufficiently high accuracy of approximation of experimental density data allows the use of equations of state to calculate not only thermal, but also caloric properties (Ganiyev, Abbasov, 2009; Polyak, 2009).

As was clear from equation (3), the dependences A (T) for the indicated system are parallel, almost close to each other, which is very important for their generalization. The dependence of B (T) on temperature T is also close to each other and has a similar form.

This opens up the possibility, with a successful choice of the method of reducing functions to a dimensionless form, to obtain a single generalized form of the temperature functions of the equation of state in the form (2).

Studies of various options and methods for generalizing the temperature functions A (T) and B (T) of the equation of state indicate that favorable results can be obtained if you use dimensionless coordinates in the following form:

$$\frac{A}{A_н}\left(\frac{T}{T_н}\right) = F_1\left(\frac{T}{T_H}\right) \text{ и } \frac{B}{B_n}\left(\frac{T}{T_H}\right) = F_2\left(\frac{T}{T_H}\right) \qquad (4)$$

where $T_H = T_{H1} \cdot (1 - x) + T_{H2} \cdot X$; here T_H1 and T_H2 are the normal boiling temperatures of the first and second components, respectively, that make up the mixture: x is the relative mass for the second component.

For scientific systems, we found the values of function coefficients using the least squares method.

$$\frac{A}{A_H}\left(\frac{T}{T_H}\right) = \sum_{i=0}^{3} C_i \left(\frac{T}{T_H}\right)^i \qquad (5)$$

$$\frac{B}{B_H}\left(\frac{T}{T_H}\right) = \sum_{i=0}^{3} d \left(\frac{T}{T_H}\right)^i \qquad (6)$$

included in the generalized equation of state, having the form:

$$P = \frac{A}{A_H}\left(\frac{T}{T_H}\right) \cdot A_H \cdot T_H \cdot \rho^2 + \frac{B}{B_n}\left(\frac{T}{T_H}\right) \cdot B_H \cdot T_H \cdot \rho^2 \qquad (7)$$

Further analysis of the behavior of A_n (T_N) and B_n (T_H) showed that the values of these quantities can be expressed by a relatively simple function of the conditional normal boiling point TN. These dependencies were approximated by simple equations:

$$\left.\begin{aligned} A_H(T_H) &= \sum_{i=0}^{2} K_i \cdot T_H^i \\ B_H(T_H) &= \sum_{i=0}^{2} l_i T_H^i \end{aligned}\right\} \quad (8)$$

Now, the finally generalized equation of state for the studied systems has the form: (Mustafaev, Ganiev, 1981).

$$P = \frac{1}{v^2}\left[\sum_{i=0}^{2} K_i \cdot T_H^i \cdot \sum_{i=0}^{2} C_i \left(\frac{T}{T_k}\right)^i\right] + \frac{1}{v^8}\left[\sum_{i=0}^{2} l_i T_H^i \cdot \sum_{i-0}^{2} d_i \left(\frac{T}{T_H}\right)^i\right] \quad (9)$$

Using this equation, it is possible to determine with satisfactory accuracy the density of substances, even mixtures, at various pressures, temperatures and concentrations.

The program of this study provided for the determination of a set of thermophysical properties based on minimal experimental information.

Checking our proposed individual equations of state showed that they are quite suitable for calculating thermal properties.

Thermal expansion

$$\alpha_p = -\frac{1}{\rho}\left(\frac{d\rho}{dT}\right)_P \text{ и } \beta_T = \frac{1}{\rho}\left(\frac{d\rho}{dP}\right)_T \quad (10)$$

From equation (2) we get:

$$\alpha_p = -\frac{1}{\rho}\left(\frac{d\rho}{dT}\right)_P = -\frac{A'(T)+B'(T)\cdot\rho^6}{2\cdot A(T)+8B(T)\cdot\rho^8} \quad (11)$$

$$\beta_T = \frac{1}{\rho}\left(\frac{d\rho}{dP}\right)_T = \frac{1}{2\cdot A(T)\cdot\rho^2+8B(T)\cdot\rho^8} \quad (12)$$

Equation (2) also allows you to calculate the value of internal pressure (Pi) and the difference in heat capacities CP – CV using the following thermodynamic relationships: (Mustafaev, Ganiev, 1981; Ganiyev, Abbasov, 2010).

$$P_i = \frac{\alpha_P}{\beta_T}\cdot T - P \quad (13)$$

$$C_p - C_V = \frac{\alpha_P^2\cdot T}{\beta_T\cdot\rho} \quad (14)$$

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