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EQUATION OF STATE OF SALICYLATES

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An equation of state for salicylates is compiled that describes experimental data on density within the accuracy of the experiment.

In our previous works we presented results of an experimental study of the P-ρ-T relation of esters, namely, salicylates (methyl-, amyl-, and hexylsalicylate), over the range of temperatures from room to 573.15 K and pressures up to 60 MPa [1, 2]. The study was conducted using the method of hydrostatic weighing with a maximum error of 0.1% over the entire investigated region of state parameters.

The present work is devoted to setting up an equation of state for salicylates.

The development of an equation of state that is based on experimental P-ρ-T data and that describes thermodynamic properties of actual substances over a wide range of state parameters is of great scientific importance. In recent times definite progress has been made along these lines. In spite of this, thus far, theory has failed to suggest a satisfactory description of the properties of fluids [3, 4]. Therefore, frequently one is led to use empirical and semiempirical equations [5, 6] whose coefficients are determined from experimental P-ρ-T data. This is explained by the fact that the procedure for forming an equation of state on the basis of thermal properties has been worked out to a quite satisfactory extent and moreover it is possible to obtain more exact data on the P-ρ-T relation by an experimental approach than from caloric properties.

In forming an equation of state, particular attention is devoted to the accuracy in describing the initial data, as well as to the ease and convenience of applying the equation. For this purpose, from a considerable number of empirical equations of state we considered those that are most worthy of mention (the equations given by Tate, Bachinskii, Biron-Mamedov, and Planck). It has been established that none of these can describe satisfactorily the density of the fluids examined by us over the entire investigated range of temperatures and pressures.

We found that the equation of state suggested in [7, 8] is the best one for describing the experimental data on the density:

$$P = \frac{K}{\vartheta^m} + \frac{L}{\vartheta^n}. \tag{1}$$

A study of equation of state (1) on a computer has revealed the optimum values of m and n at which the experimental data on the density of salicylates are described with the least uncertainty. Table 1 contains the values of m and n for each ester. Their molecular masses are also given in this table. We can see from the table that for all the salicylates investigated $m = 1$, whereas n increases with an increase in the molecular mass.

Thus, the equation of state for salicylates has the form

$$P = K(T)\rho + L(T)\rho^n. \tag{2}$$

The dependences of K and L on temperature for all three fluids examined are presented in Fig. 1. These dependences are approximated by polynomials of the following form with high accuracy using the least-squares method on a computer:

$$K(T) = \sum_{i=0}^{N} k_i T^i; \quad L(T) = \sum_{i=0}^{N} l_i T^i, \tag{3}$$

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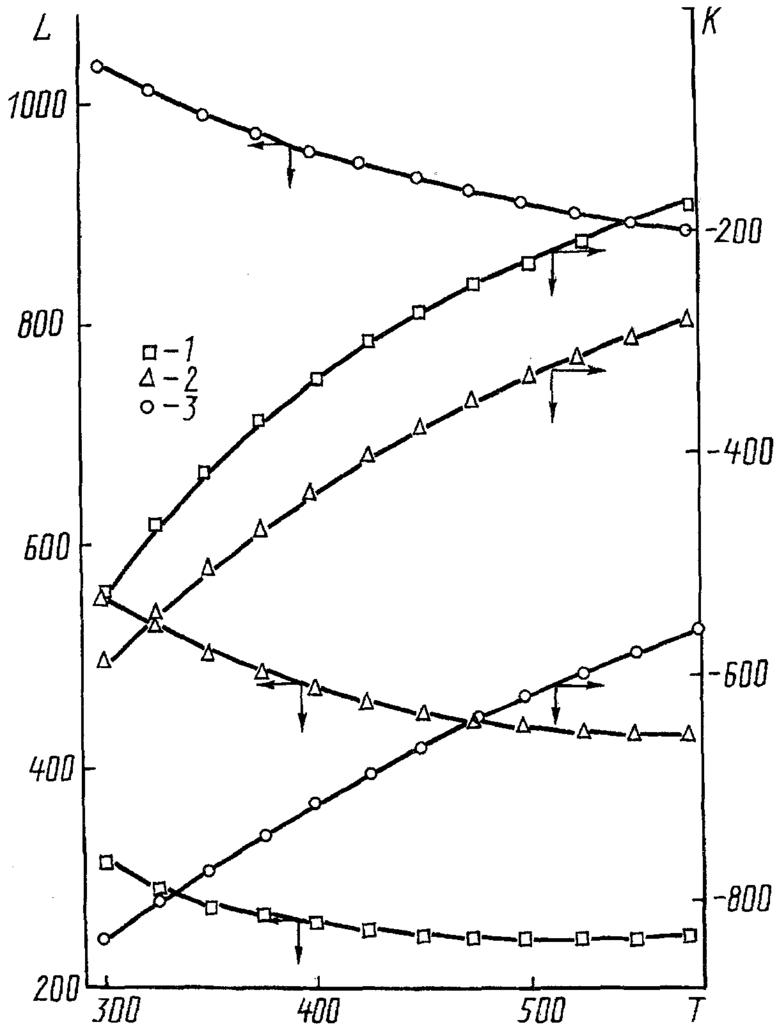

Fig. 1. Functions $K = f(T)$ and $L = f(T)$ for the test esters: 1) methylsalicylate, 2) amylsalicylate; 3) hexylsalicylate. T, K.

TABLE 1

Salicylates	M	m	n
Hexylsalicylate	222.26	1	2
Amylsalicylate	208.26	1	3
Methylsalicylate	152.15	1	4

where $N = 2$ for hexylsalicylate, $N = 3$ for amylsalicylate, and $N = 6$ for methylsalicylate. The values of the coefficients k_i and l_i for each fluid are given in Table 2.

To estimate the accuracy of the analytical description of the data by equation of state (2), in Fig. 2 we plotted graphs of the deviations in the density values for salicylates from those calculated by equation of state (2). From this figure it is seen that equation of state (2) describes experimental data on the density of salicylates mainly with the accuracy of the experiment. The maximum error attains 0.2% at three points (for methylsalicylate at $T = 450.15$ and 475.15 K and $P = 0.1$ MPa; for amylsalicylate at $T = 525.15$ K and $P = 0.1$ MPa).

Thus, from the entire data file (252 points) entered into the computer for setting up an equation of state, only three points attain the error of ±0.2% at $P = 0.1$ MPa.

It should be noted that using the proposed equation of state and well-known thermodynamic relations it is possible to calculate all necessary thermodynamic properties of the esters investigated.

TABLE 2

k_i	l_i	k_i	l_i
Hexylsalicylate		Methylsalicylate	
$k_0=-1315.567$	$l_0=1390.356$	$k_0=-2481.008$	$l_0=1116.165$
$k_1=1.965474$	$l_1=-1.524829$	$k_1=7.971381$	$l_1=-3.284566$
$k_2=-1.130000\cdot10^{-3}$	$l_2=1.126933\cdot10^{-3}$	$k_2=8.565519\cdot10^{-3}$	$l_2=-4.211153\cdot10^{-3}$
		$k_3=-5.952877\cdot10^{-5}$	$l_3=2.809078\cdot10^{-5}$
Amylsalicylate		$k_4=1.861396\cdot10^{-8}$	$l_4=-8.224466\cdot10^{-9}$
		$k_5=1.480076\cdot10^{-10}$	$l_5=-7.254168\cdot10^{-11}$
$k_0=-1749.665$	$l_0=-3.382407$	$k_6=-1.419861\cdot10^{-13}$	$l_6=7.004250\cdot10^{-14}$
$k_1=6.327292$	$l_1=-3.382407$		
$k_2=-9.822468\cdot10^{-3}$	$l_2=5.210155\cdot10^{-3}$		
$k_3=5.675489\cdot10^{-6}$	$l_3=-2.677925\cdot10^{-6}$		

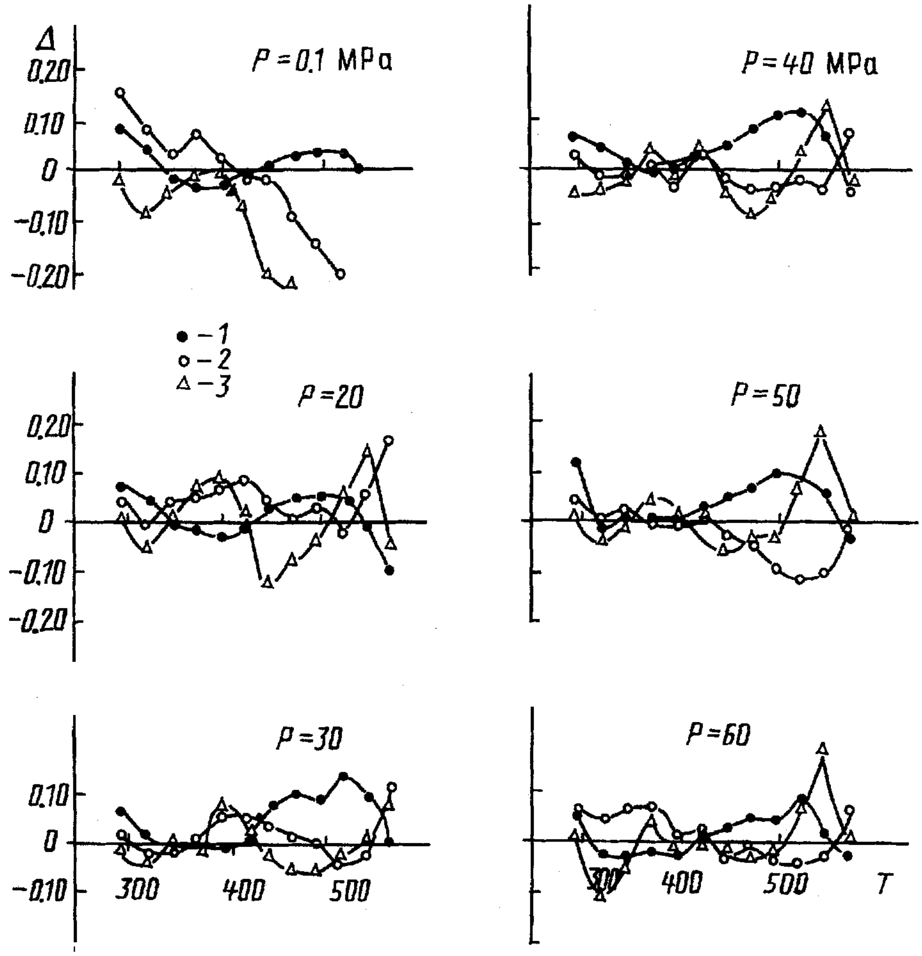

Fig. 2. Deviations of experimental values of the density of salicylates from those calculated by the state equation: 1) hexylsalicylate, 2) amylsalicylate, 3) methylsalicylate. Δ, %.

NOTATION

P, external pressure; ϑ, specific volume; ρ, density; K and L, coefficients depending on the temperature; m and n, positive integral numbers; M, molecular weight.

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