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GENERALIZED EQUATION OF STATE OF ETHERS

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An equation of state is obtained on the basis of experimental data on the density of liquid ethers over the temperature range 293-584 K and the pressure range 0.1-98.1 MPa.

Despite widespread use of ethers, their density remains little investigated. Taking this into account, we have measured the density of liquid ethers (diethyl, diallyl, dipropyl, diamyl, dihexyl, diheptyl, dioctyl) over the temperature range 293-584 K and the pressure range 0.1-98.1 MPa. The measurements were performed by the method of hydrostatic weighing [1]. The total relative measurement error for density is 0.1%.

It is established that with increasing temperature the influence of pressure on the value of density for liquid ethers increases. For example, whereas a change of pressure from 4.91 to 98.1 MPa at a temperature of 293 K increases the density of liquid diethyl ether by 8.4% then at a temperature of 561 K this increase is 19.7%.

To obtain an equation of state for liquid ethers using experimental data at various temperatures and pressures, the lines T = const were constructed in the plane $(P/\rho^2RT - 1/\rho), \rho^6$ [2-5]:

$$\frac{P}{\rho^2 RT} = 1 + B\rho + A\rho^7. \tag{1}$$

Figure 1 shows the feasibility of the dependence (1) for the investigated diheptyl ether. As is shown in Fig. 1, the lines T = const are straight and are described by the equation

$$Z = 1 + B\rho + A\rho^7, \tag{2}$$

where $Z = P/\rho RT$ is the compressibility of the objects in question, given T and P; P is the external pressure, Pa; ρ is the density, kg/m^3; A and B are coefficients; R is the gas constant of the ethers, J/(kg·K).

Analysis of the coefficients A and B has shown that they are functions of temperature, i.e., $A = f_1(T)$ and $B = f_2(T)$. Therefore we will write Eq. (2) in the following form (Figs. 2 and 3):

$$Z = 1 + B(T)\rho + A(T)\rho^7. \tag{3}$$

Knowing the dependences $f_1(T)$ and $f_2(T)$, from Eq. (3) one can calculate the density of the ethers over a wide range of temperatures and pressures.

The coefficients A(T) and B(T) are calculated for each isotherm by a least-squares method and then on the basis of graphoanalytical analysis are approximated with an error of 0.11% by second-power polynomials:

$$A(T) = \sum_{i=0}^{2} a_i T^i; \quad B(T) = \sum_{i=0}^{2} b_i T^i. \tag{4}$$

The temperature dependence of a_i and b_i is given in Table 1.

In view of (2)-(4) we will give Eq. (1) so:

$$Z = 1 + \sum_{i=0}^{2} b_i T^i \rho + \sum_{i=0}^{2} a_i T^i \rho^7. \tag{5}$$

A check of the equation of state (5) has shown that it describes the experimental data on the density of the ethers in question with an error of 0.09%. On the basis of Eq. (5) we calculated the volumetric expansion α_p and isothermal

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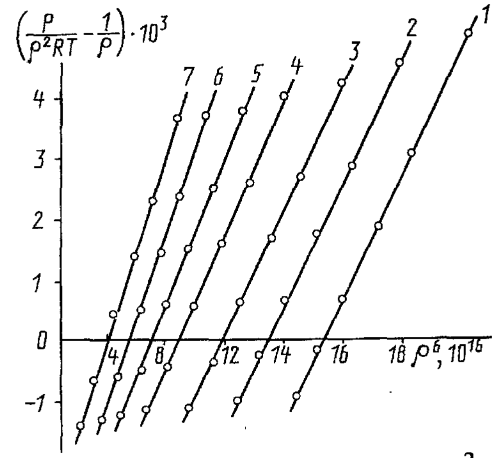

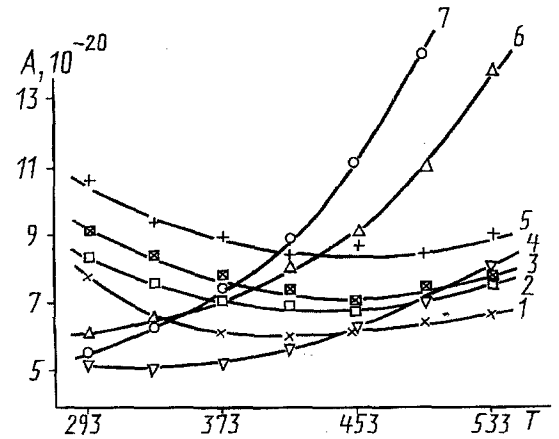

Fig. 1. Dependence of $(P/\rho^2 RT - 1/\rho)$, m^3/kg, on ρ^6, kg^6/m^{18}: 1) 300; 2) 333; 3) 373; 4) 393; 5) 413; 6) 453; 7) 493.

Fig. 2. Dependence of A, m^{21}/kg^7, on T, K: 1) diethyl; 2) diallyl; 3) dipropyl; 4) diamyl; 5) dihexyl; 6) diheptyl; 7) dioctyl.

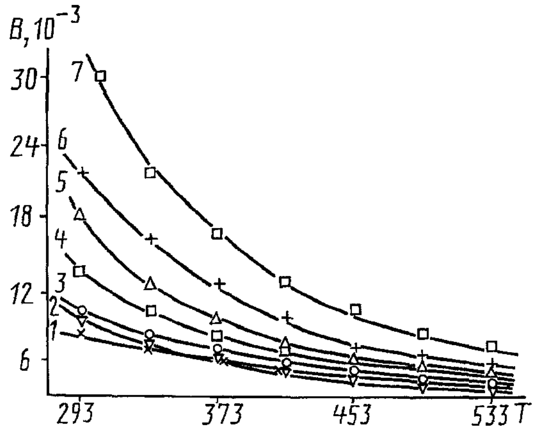

Fig. 3. Dependence of B, m^3/kg, on T. The notation is the same as in Fig. 2.

TABLE 1. Coefficients a_i and b_i of Eq. (5) for the Investigated Ethers

Ether	Values of coefficients					
	a_1	a2	a3	b1	b2	b3
Diethyl	$2.27\cdot10^{-24}$	$-1.3574\cdot10^{-21}$	$2.6059\cdot10^{-19}$	5.1780·10-8	$-6.0288\cdot10^{-5}$	$2.2061\cdot10^{-2}$
Diallyl	$1.390\cdot10^{-24}$	$-8.4065\cdot10^{-22}$	$1.8914\cdot10^{-19}$	$1.1063\cdot10^{-7}$	$-1.1426\cdot10^{-4}$	3.4309·10-2
Dipropyl	$5.9671\cdot10^{-25}$	$-3.6315\cdot10^{-22}$	$1.0667\cdot10^{-19}$	$1.0803\cdot10^{-7}$	-1.1446·10-4	3.3936·10-2
Diamyl	$8.9579\cdot10^{-25}$	$-7.6707\cdot10^{-22}$	$2.2384\cdot10^{-19}$	$6.9564\cdot10^{-7}$	-6.2469·10-4	1.3756·10-1
Dihexyl	$8.799\cdot10^{-25}$	$-7.55\cdot10^{-22}$	$2.29\cdot10^{-19}$	$3.0578\cdot10^{-7}$	-3.2088·10-4	8.9752·10-2
Diheptyl	$8.863\cdot10^{-25}$	$-7.693\cdot10^{-22}$	$2.343\cdot10^{-19}$	$3.634\cdot10^{-7}$	-3.347·10-4	9.647·10-2
Dioctyl	$9.2257\cdot10^{-25}$	$-8.2812\cdot10^{-22}$	$2.6931\cdot10^{-19}$	$3.9143\cdot10^{-7}$	-4.1574·10-4	1.1789·10-1

compressibility β_T coefficients from the dependences

$$\alpha_p = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_p = \frac{A'(T) + B'(T)\rho^6}{2A(T) + 8B(T)\rho^6}, \tag{6}$$

$$\beta_T = \frac{1}{\rho}\left(\frac{\partial\rho}{\partial p}\right)_T = \frac{1}{2\rho^2 A(T) + 8\rho B(T)}. \tag{7}$$

Next, knowing α_p and β_T, we calculated the internal pressure P_i, the heat capacity difference $(C_p - C_v)$, and the thermal pressure γ of the liquids in question:

$$P_i = \frac{\alpha_p}{\beta_T} T - P, \tag{8}$$

$$C_p - C_v = \frac{\alpha_p^2 T}{\beta_T \rho}, \tag{9}$$

$$\gamma = \frac{1}{P} [A'(T) \rho^2 + B'(T) \rho^8]. \tag{10}$$

With increasing temperature the coefficients of volumetric expansion and isothermal compressibility and the heat capacity difference increase, and with increasing pressure decrease.

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