A GENERAL EQUATION FOR THE DYNAMIC VISCOSITY OF A BINARY MIXTURE OF ORGANIC LIQUIDS OVER A WIDE RANGE IN STATE PARAMETERS

R. A. Mustafaev and D. K. Ganiev UDC 532.1.133

Experimental data have been used in a general equation for the dynamic viscosity of a binary system as a function of temperature, pressure, and concentration.

In the design of equipment for making or using n-butyraldehyde, isobutyraldehyde, n-butanol, or isobutanol, or mixtures of various compositions, it is necessary to have reliable information on the thermophysical parameters.

Unfortunately, at present we do not have reliable methods of predicting the thermophysical parameters of substances, especially polyatomic and polar compounds, which include the above substances and their mixtures. Therefore, we have performed experiments [1-3] to determine the dynamic viscosities of major binary systems consisting of normal and isomeric aldehydes and alcohols differing considerably in physical properties. We used a capillary viscometer in Golubev's form [4-6].

The measurements covered the ranges 290-505°K and 0.1-58.9 MPa.

The experimental data [1,3] show that T = const lines in the η-P diagram represent the simplest relationships for all substances and mixtures over wide ranges in pressure and temperature. Figure 1 shows this for a mixture of n-butanol with isobutanol; the same form applies for the other systems. The viscosity data can then be represented as

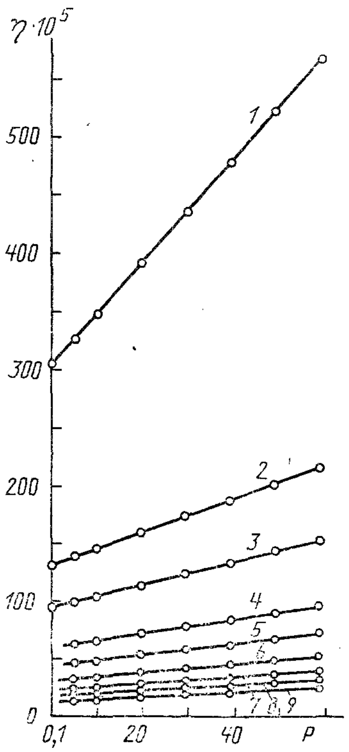

Fig. 1. Effects of pressure on the viscosity of a mixture of 80% n-butanol + 20% isobutanol along the following isotherms: 1) T = 294.63°K; 2) 328.13; 3) 343.53; 4) 368.58; 5) 387.33; 6) 413.73; 7) 442.33; 8) 469.88; 9) 502.80. η in Pa·sec and P in MPa.

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TABLE 1. Values of n_i and m_i in (1) for the System Formed by n-Butanol with Isobutanol

Coefficients	Substance			
	n-butanol	isobutanol	88% n-butanol+12% isobutanol	80% n-butanol+ 20% isobutanol
n_0	$-2,01146\cdot10^{1}$	$-3,61609\cdot10^{1}$	$-2,15387\cdot10^{1}$	$-2,30376\cdot10^{1}$
n_1	$3,03184\cdot10^{4}$	$5,33296\cdot10^{4}$	$3,19092\cdot10^{4}$	$3,41139\cdot10^{4}$
n_2	$-1,57164\cdot10^{7}$	$-2,82838\cdot10^{7}$	$-1,65549\cdot10^{7}$	$-1,77662\cdot10^{7}$
n_3	$3,83937\cdot10^{9}$	$6,84739\cdot10^{9}$	$4,03031\cdot10^{9}$	$4,32251\cdot10^{9}$
n_4	$-3,45837\cdot10^{11}$	$-6,09031\cdot10^{11}$	$-3,61238\cdot10^{11}$	$-3,87107\cdot10^{11}$
m_0	$-4,77438\cdot10^{1}$	$4,26224\cdot10^{1}$	$-2,37284\cdot10^{1}$	$-1,65654\cdot10^{1}$
m_1	$7,65932\cdot10^{4}$	$-7,89006\cdot10^{4}$	$3,66294\cdot10^{4}$	$2,41664\cdot10^{4}$
m_2	$-4,73007\cdot10^{7}$	$5,07398\cdot10^{7}$	$-2,27309\cdot10^{7}$	$-1,47902\cdot10^{7}$
m_3	$1,27980\cdot10^{10}$	$-1,41231\cdot10^{10}$	$6,17394\cdot10^{9}$	$3,97071\cdot10^{9}$
m_4	$-1,25488\cdot10^{12}$	$1,47086\cdot10^{12}$	$-5,93628\cdot10^{11}$	$-3,68046\cdot10^{11}$

TABLE 2. Values of n_i and m_i in (1) for the System Formed by n-Butyraldehyde with Isobutyraldehyde

Coefficients	Substance			
	n-butanol	isobutanol	88% n-butanol + 12% isobutanol	80% n-butanol + 20% isobutanol
n_0	$-3,56684\cdot10^{0}$	$-5,96063\cdot10^{1}$	$-1,67630\cdot10^{1}$	$-1,23829\cdot10^{1}$
n_1	$6,18956\cdot10^{3}$	$8,63698\cdot10^{4}$	$2,53598\cdot10^{4}$	$1,88071\cdot10^{4}$
n_2	$-1,66053\cdot10^{6}$	$-4,45714\cdot10^{7}$	$-1,20034\cdot10^{7}$	$-8,42375\cdot10^{6}$
n_3	$1,82287\cdot10^{8}$	$1,03440\cdot10^{10}$	$2,63881\cdot10^{9}$	$1,787\cdot10^{9}$
n_4	—	$-8,97897\cdot10^{11}$	$-2,16846\cdot10^{11}$	$-1,42213\cdot10^{11}$
m_0	$1,66790\cdot10^{0}$	$2,60551\cdot10^{1}$	$3,50009\cdot10^{1}$	$6,64638\cdot10^{0}$
m_1	$-1,68364\cdot10^{3}$	$-3,78893\cdot10^{4}$	$-5,05896\cdot10^{4}$	$-9,08264\cdot10^{3}$
m_2	$3,63561\cdot10^{5}$	$2,02042\cdot10^{7}$	$2,68653\cdot10^{7}$	$4,42394\cdot10^{6}$
m_3	$1,40795\cdot10^{7}$	$-4,75089\cdot10^{9}$	$-4,75089\cdot10^{9}$	$-9,62741\cdot10^{8}$
m_4	—	$4,24161\cdot10^{11}$	$5,54989\cdot10^{11}$	$8,71219\cdot10^{10}$

TABLE 3. Values of n_i and m_i in (1) for the System Formed by n-Butanol with n-Butyraldehyde

Coefficients	Substance		
	90% n-butanol 10% butyraldehyde	60% n-butanol+40% butyraldehyde	10% n-butanol+90% butyraldehyde
n_0	$-1,81492\cdot10^{1}$	$-1,13222\cdot10^{1}$	$-4,65587\cdot10^{0}$
n_1	$2,72745\cdot10^{4}$	$1,74463\cdot10^{4}$	$7,74503\cdot10^{3}$
n_2	$-1,39742\cdot10^{7}$	$-8,22788\cdot10^{6}$	$-2,54057\cdot10^{6}$
n_3	$3,37745\cdot10^{9}$	$1,86721\cdot10^{9}$	$3,98197\cdot10^{8}$
n_4	$-3,00353\cdot10^{11}$	$-1,54759\cdot10^{11}$	$-1,86170\cdot10^{10}$
m_0	$-4,38731\cdot10^{0}$	$-3,23339\cdot10^{1}$	$-2,84506\cdot10^{0}$
m_1	$7,08436\cdot10^{4}$	$5,21280\cdot10^{4}$	$5,41779\cdot10^{3}$
m_2	$-4,37463\cdot10^{7}$	$-3,18007\cdot10^{7}$	$-3,38418\cdot10^{6}$
m_3	$1,17937\cdot10^{10}$	$8,43200\cdot10^{9}$	$1,10024\cdot10^{9}$
m_4	$-1,15005\cdot10^{12}$	$-8,06089\cdot10^{11}$	$-1,02198\cdot10^{11}$

$$\eta = L(T) + K(T)P. \quad (1)$$

The temperature dependence L(T) and K(T) shows that these functions are similar for the various compositions and can be described by the equations

$$L(T) = \exp\left(\sum_{i=0}^{4} \frac{n_i}{T^i}\right), \quad (2)$$

$$K(T) = \exp\left(\sum_{i=0}^{4} \frac{m_i}{T^i}\right). \quad (3)$$

Tables 1-3 give the n_i and m_i found by least-squares fitting for the three systems.

The calculations and comparisons show that (1) with the coefficients in the tables fits the measurements with a mean deviation in the range 0.5-0.7%.

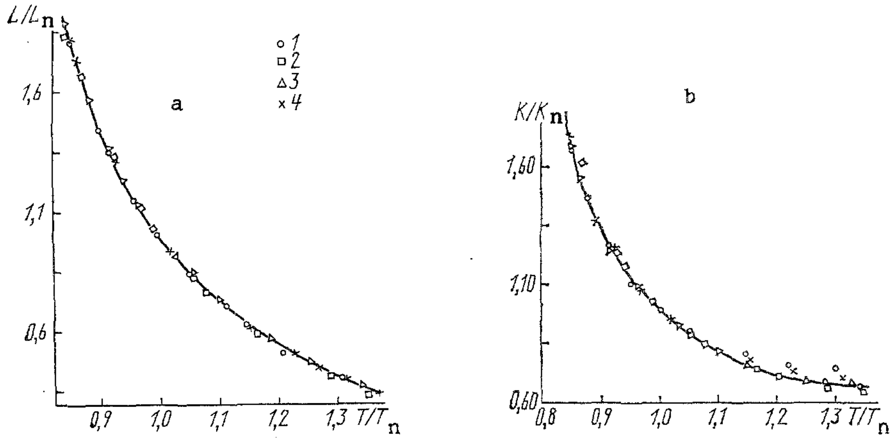

Fig. 2. Dependence of L/L_n (a) and K/K_n (b) on T/T_n for the system formed by n-butyraldehyde with isobutyraldehyde: 1) n-butyraldehyde; 2) isobutyraldehyde; 3) 88% n-butyraldehyde + 12% isobutyraldehyde; 4) 80% n-butyraldehyde + 20% isobutyraldehyde.

TABLE 4. Values of ϕ_{1i} and ϕ_{2i} in (5) and (6)

Coefficients	Systems		
	n-butyraldehyde with isobutyraldehyde	n-butanol with n-butyraldehyde	n-butanol with isobutanol
φ_{10}	$-5{,}05610\cdot10^{0}$	$1{,}215276\cdot10^{2}$	$-8{,}72578\cdot10^{0}$
φ_{11}	$1{,}98638\cdot10^{2}$	$-6{,}137209\cdot10^{2}$	$-6{,}41331\cdot10^{0}$
φ_{12}	$-3{,}02050\cdot10^{2}$	$1{,}192799\cdot10^{3}$	$-7{,}91108\cdot10^{1}$
φ_{13}	$2{,}06797\cdot10^{2}$	$-1{,}130138\cdot10^{3}$	$-1{,}32926\cdot10^{2}$
φ_{14}	$-5{,}28335\cdot10^{1}$	$5{,}250166\cdot10^{2}$	$9{,}19934\cdot10^{1}$
φ_{15}	—	$-9{,}547195\cdot10^{1}$	$-2{,}30333\cdot10^{1}$
φ_{20}	$7{,}26786\cdot10^{0}$	$1{,}960413\cdot10^{1}$	$1{,}46082\cdot10^{2}$
φ_{21}	$2{,}88004\cdot10^{1}$	$-7{,}785171\cdot10^{1}$	$-7{,}92007\cdot10^{2}$
φ_{22}	$3{,}89179\cdot10^{1}$	$1{,}117271\cdot10^{2}$	$1{,}68669\cdot10^{3}$
φ_{23}	$-2{,}29322\cdot10^{1}$	$-7{,}187587\cdot10^{1}$	$-1{,}77928\cdot10^{3}$
φ_{24}	$5{,}54579\cdot10^{0}$	$-1{,}811457\cdot10^{1}$	$9{,}31142\cdot10^{2}$
φ_{25}	—	—	$-1{,}92650\cdot10^{2}$

Equation (1) is an individual one. It is desirable to formulate a general equation suitable for all these systems.

The behavior of L(T) and K(T) is such that the functions are similar in form for different compositions, so an appropriate way of reducing the functions to dimensionless form should give a single general form for (1). We reduced L(T) and K(T) to dimensionless form by referring the values to the normal boiling points:

$$\frac{L(T)}{L_n(T_n)} = F_1\left(\frac{T}{T_n}\right), \quad \frac{K(T)}{K_n(T_n)} = F_2\left(\frac{T}{T_n}\right). \tag{4}$$

In (4), $T_n = [T_{n1}(100 - x) + T_{n2}x]/100$, with T_{n1} and T_{n2} the normal boiling points correspondingly of the first and second components, while x is the percent content of the second component.

Figure 2 shows the results for the system formed by n-butyraldehyde with isobutyraldehyde; all the L and K fit a single curve closely. The equations for the general curves take the form

$$\frac{L(T)}{L_n(T_n)} = \exp\left[\sum_{i=0}^{5} \varphi_{1i}\left(\frac{T}{T_n}\right)^i\right], \tag{5}$$

$$\frac{K(T)}{K_n(T_n)} = \exp\left[\sum_{i=0}^{5} \varphi_{2i}\left(\frac{T}{T_n}\right)^i\right]. \tag{6}$$

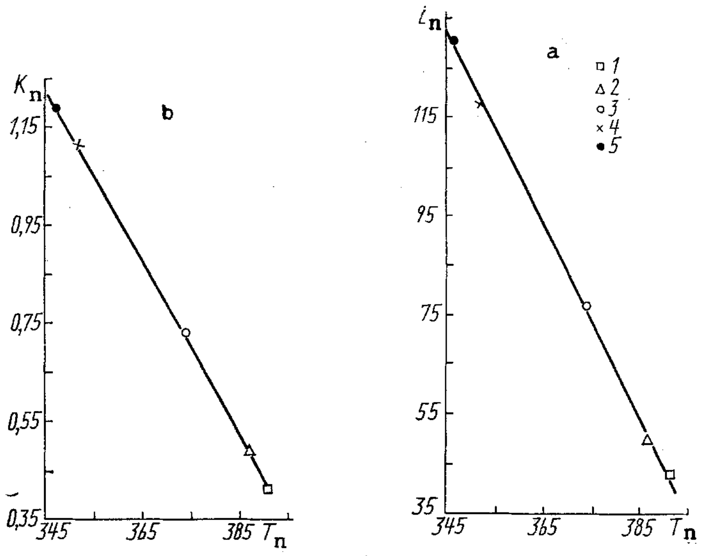

Fig. 3. Dependence of L_n (a) and K_n (b) on T_n for the system formed by n-butanol with n-butyraldehyde: 1) n-butanol; 2) 90% n-butanol + 10% n-butyraldehyde; 3) 60% n-butanol + 40% n-butyraldehyde; 4) 10% n-butanol + 90% n-butyraldehyde; 5) n-butyraldehyde; T_n in K.

TABLE 5. Values of ψ_{1i} and ψ_{2i} in (7) and (8)

Coefficients	Systems		
	n-butyraldehyde with isobutyraldehyde	n-butanol with isobutyraldehyde	n-butanol with isobutanol
ψ_{10}	$2,95650\cdot10^{0}$	$7,93798\cdot10^{2}$	$3,12189\cdot10^{2}$
ψ_{11}	$4,87773\cdot10^{1}$	$-1,92442\cdot10^{0}$	$6,89694\cdot10^{-1}$
ψ_{20}	$1,55429\cdot10^{0}$	$7,36848\cdot10^{0}$	$6,35212\cdot10^{0}$
ψ_{21}	$1,25098\cdot10^{-2}$	$-1,77906\cdot10^{-2}$	$1,52043\cdot10^{-2}$

Table 4 gives the ϕ_{1i} and ϕ_{2i} for the three two-component systems.

The $L_n(T_n)$ and $K_n(T_n)$ relationships are linear (Fig. 3) and can be fitted to the equations

$$L_n(T_n) = \psi_{10} + \psi_{11}T_n, \tag{7}$$

$$K_n(T_n) = \psi_{20} + \psi_{22}T_n. \tag{8}$$

Table 5 gives the coefficients. From (7) and (8), the general equation is

$$\eta = (\psi_{10} + \psi_{11}T_n)\exp\left[\sum_{i=0}^{5}\varphi_{1i}\left(\frac{T}{T_n}\right)^i\right] + (\psi_{20} + \psi_{22}T_n)\exp\left[\sum_{i=0}^{5}\varphi_{2i}\left(\frac{T}{T_n}\right)^i\right]P. \tag{9}$$

The maximal deviations are 2-3% for the values calculated from (9) from our measurement data.

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