The least-squares method is applied to determine the parameters in the rheological equation of state for the liquid over wide ranges in the velocity gradient and tangential stress.

The rheological parameters of liquids have major effects on the hydromechanical, thermal, and mass-transfer processes [1], and therefore correct determination of the rheological equation of state for a liquid is a basic problem in rheology [2, 3].

The ranges in strain rate and stress for a given object frequently constitute 4-6 orders of magnitude, so mathematical description of experimental values usually involves piecewise approximation for individual ranges in
the input and output parameters by means of a classical least-squares method [4, 5]. This complicates calculations related to the logical selection of an equation in relation to the range in the tangential stress or velocity gradient. There are major difficulties in describing the entire ranges in the input and output parameters by means of a single rheological equation of state. We can demonstrate this on the determination of the rheological equation of state for glycerol, which is one of the simplest Newtonian liquids:

$$\tau = \mu \gamma.$$ 

Table 1 gives results from the capillary viscometry of glycerol at \( t = 60^\circ C \).

The tangential stresses and velocity gradient were determined as functions of the pressure gradient and the corresponding flow rate from the following formulas [3]:

$$\tau_w = \frac{\Delta p}{4l} \cdot \frac{d_c}{d_c^2}; \quad \dot{\gamma}_w = \frac{32q}{\pi d_c^3}.$$ 

The viscometry results were backed up by processing the dwell-time distribution via the following equations [6]:

$$\dot{\gamma} = \frac{4l}{d_c} \cdot \left( \int_0^t C_i \dot{t} dt \right)^{0.5}; \quad \int_0^t C_i \dot{t} dt.$$ 

$$\tau = \lambda \cdot p d_c \cdot \left( \int_0^t C_i \dot{t} dt \right)^{0.5}.$$ 

The upper part of Table 1 shows that the results from the classical least-squares method for the entire ranges of input and output quantities at 60\(^\circ\)C are such that glycerol behaves as a viscoplastic liquid with a limiting shear stress \( \Theta = 0.055 \text{ N/m}^2 \).

The coefficients in the rheological equation of state obtained by this method

$$(\tau \cdot 10^3) = 55 + 104.9 \dot{\gamma}$$

were examined on Student's t-test, which demonstrated significance for both coefficient [7]. This conclusion that glycerol is a viscoplastic liquid conflicts with the evidence that it is a Newtonian liquid. Also, there are impermissibly large relative deviations between the theoretical and experimental values for the tangential stresses at low velocity gradients, which indicates either an error in the experiment or that the entire range of the input and output parameters cannot be fitted to a single equation by least squares.

In our view, this occurs because the criterion for minimizing the sum of the squares of the deviation in the least-squares method

$$S_1^2 = \sum_{i=1}^{n} [(b + ax_i) - y_i]^2 \text{min}$$

(1)

gives good results when the experimental data relate to narrow ranges in the input and output parameters.

If the ranges in the input and output parameters are wide, the least-squares approximation gives an unsatisfactory result because the theoretical and observed values of the function come together in absolute magnitude in the region of their largest numerical values at one end of the range of measurement, where (1) shows that one obtains the least squares of the deviations. On the other hand, at the other end of the range of the measurements, namely at small numerical values for the function [where the deviations in absolute magnitude are small and make the least contribution to the sum in (1)], the relative deviations between the theoretical and experimental values may be hundreds or thousands of percent (Table 1).

Therefore, to approximate the data over wide ranges in the parameters it is desirable for condition (1) to be replaced by a condition in which one minimizes the sum of the relative squares of the deviations: