THERMOPHYSICAL PROPERTIES
OF MATERIALS

Peculiarities of Temperature Dependence of Liquid 1-Chloroalkane Viscosity

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Abstract—Experimental values are presented for the 1-chloroalkanes viscosity within the temperature range of 253.15–423.15 K, obtained by means of standard quartz viscometer. According to investigation results, grounded suppositions and generalizations are made concerning temperature dependence characteristics of the dynamic viscosity of 1-chloroalkanes.

INTRODUCTION

Viscosity is one of the most important parameters characterizing the nature of the internal structure and the intermolecular forces in liquids. Thus, data on the viscosity are of undoubted interest to the physics of fluids and statistical thermodynamics. In particular, these data might be applied to estimate the degree of reliability of the existing liquid models.

Data on liquid viscosity are also of important application significance and are necessary to estimate the efficiency of various technological processes and procedures such as filtration, sedimentation, mass and heat exchange, and transportation of the liquids.

The present work is part of a program on the investigation of thermophysical properties of monohalogenalkanes and their binary mixtures with alkanes performed in the Laboratory for Molecular Acoustics, Condensed State Physics R&D Center, Kursk State University. In previous publications [1−7], we present the results of measurements of the sound velocity, the density, and some other values characterizing the thermophysical properties of the liquid monohalogenalkanes and their mixtures and draw a conclusion on the peculiarities of the intermolecular forces in organic liquids with an open-chain structure of molecules.

EXPERIMENT

For the studies, we took liquid 1-chloroalkanes granted by the Sigma-Aldrich Ltd. The molar fraction of the main substance was at least 98%. We did not perform any additional purification of the specimens. We tested the liquid purity before and after the viscosity measurements by measuring its density and refractive index. Before the viscosity measurements, for the degassing, we subjected the specimens to prolonged centrifugation.

We measured the kinematic viscosity at the atmospheric pressure within the temperature range of 253.15–423.15 K, by means of a viscometer with an internal capillary diameter of 0.73 mm. We placed the viscometer into the VIS-T (Termex, Russia) thermostat and fixed it in vertical position. In the thermostat, we maintained a constant temperature within the accuracy of ±0.01 K and controlled it by means of a 100-Ω platinum resistive thermometer with an error of ±0.001 K. We measured the liquid effluence duration (with error of 0.01 s) within a wide range, from 15 s to 200 s. When calculating the kinematic viscosity, we used the averaged value of the effluence duration estimated over 10 measurements. The scatter of the experimental values of the effluence duration at each temperature was within 0.1%. We calculated the viscosity according to the formula

$$\nu = At - B/t, \qquad (1)$$

where ν is the kinematic viscosity, t is the liquid effluence duration, and $A = 0.030757$ m^2 s^{-2} and $B = 1.33033$ m^2 are the constant viscometer parameters determined in the calibration process. The second term in (1) is a correction [8] for the kinetic energy of liquid flowing through the capillary.

To calibrate the viscometer at the operation temperatures, we engaged high-pure hexane (99.85% mol.) and toluene (99% mol.). We took the hexane and the toluene viscosity values from [9−13]. The estimated uncertainty of the experimental viscosity values was 1−2%.

RESULTS AND DISCUSSION

We used the experimental values of 1-chloroalkane kinematic viscosity combined with density data [14] to calculate the dynamic viscosity

$$\eta = \nu \rho. \qquad (2)$$

Table 1. Viscosity of 1-chloroalkanes (Pa s) at atmospheric pressure

T, K	Homolog number						
	4	5	7	8	9	10	14
253.15	0.747	1.032	2.010	2.908		5.547	
258.15	0.695	0.949	1.793	2.549		4.697	
263.15	0.651	0.877	1.613	2.255		4.027	
268.15	0.611	0.815	1.460	2.012		3.492	
273.15	0.577	0.760	1.331	1.808		3.058	
278.15	0.546	0.712	1.220	1.637		2.702	
283.15	0.517	0.669	1.124	1.490		2.407	
288.15	0.492	0.631	1.040	1.364		2.160	5.189
293.15	0.468	0.596	0.966	1.255	1.5457	1.951	4.521
298.15	0.446	0.565	0.901	1.160	1.4141	1.772	3.975
303.15	0.426	0.536	0.843	1.076	1.2992	1.619	3.524
308.15	0.407	0.510	0.791	1.002	1.1985	1.486	3.147
313.15	0.389	0.485	0.744	0.936	1.1096	1.370	2.829
318.15	0.372	0.463	0.702	0.877	1.0309	1.268	2.559
323.15	0.356	0.442	0.664	0.825	0.9609	1.178	2.327
328.15	0.340	0.422	0.629	0.777	0.8983	1.098	2.126
333.15	0.326	0.404	0.597	0.734	0.8421	1.027	1.952
338.15	0.311	0.387	0.567	0.694	0.7914	0.963	1.800
343.15		0.371	0.540	0.659	0.7455	0.905	1.666
348.15		0.356	0.515	0.626	0.7038	0.853	1.547
353.15		0.342	0.492	0.596	0.6658	0.805	1.441
358.15		0.328	0.470	0.568	0.6310	0.762	1.346
363.15		0.315	0.450	0.542	0.5991	0.723	1.261
368.15				0.518	0.5696	0.686	1.184
373.15				0.496	0.5424	0.653	1.115
378.15				0.475		0.622	1.051
383.15				0.456		0.594	0.994
388.15				0.438		0.567	0.941
393.15				0.421		0.543	0.892
398.15							0.847
403.15							0.806
408.15							0.768
413.15							0.732
418.15							0.699
423.15							0.668

Thus obtained dynamic viscosity values are presented in Table 1. Within the errors, these data are in agreement with the results [15, 16]. The existing minor discrepancies in the viscosity values are possibly caused by different purity degrees of the used liquid specimens.

Study of the temperature dependence of dynamic viscosity is of principal significance as it provides the

possibility to estimate the peculiarities of the intermolecular force and the internal structure of the liquid. To describe this dependence, a great many relations of various kinds, empirical and semi-empirical, are proposed [15−17]. The authors [16, 17] consider the relation

$$1/\eta = 1/\eta_0 \exp(-E/RT) \qquad (3)$$

to be the most well grounded.

This simple (in form) equation reflects the nature of the temperature dependence of liquid viscosity in general. The E value in (3), called the activation energy of the viscous flow, represents an individual liquid characteristic and depends on the peculiarities of its structure and the nature of the intermolecular forces. Yet, Eq. (3) does not provide the necessary exactness of the measurement result reproduction and thus the temperature dependence of the viscosity is usually represented as polynomial

$$\ln(\eta) = A + B/(C - T) + D\ln(T) + ET^F. \qquad (4)$$

The polynomial coefficients are determined by means of experimental data processing. Equation (4) provides the necessary exactness of description of the temperature dependence of liquid viscosity but loses the physical attraction inherent in (3).

The performed investigations give rise to the conclusion that, to describe the thermophysical properties of organic liquids within a wide range of state parameters, including the critical region, it is sufficient to take into account the presence of the three types of intermolecular forces: the London dispersion attraction force caused by the virtual dipole interaction; the repulsion forces resulting from the electron shell overlapping in the atoms; and the weak far-ranging "chemical" forces of the donor-acceptor type bonds responsible for the cluster structure of the liquid and postulated in [18−20]. Such concepts coincide totally with the results obtained in investigations of the biological structures [21]. According to the results [19, 20], these complexes (clusters) represent the dimeric creatures. In the direct vicinity of the critical point, they decay intensively, thus resulting in large density fluctuations causing the different effects accompanying the critical liquid−vapor transition. The energy necessary for such dimeric complex destruction is proportional to the critical temperature and is an individual substance characteristic.

To our mind, the viscosity depends on the mechanical strength of the liquid and is related to the destruction peculiarities of the complexes existing in the liquid. Under that condition, the activation energy will be proportional to the energy needed for their destruction. The presented concepts predetermine the form of the relation characterizing the temperature dependence of liquid viscosity. Here, we propose the empirical expression where a certain characteristic temperature represents the activation energy and is proportional to it. Thus, the temperature dependence of the
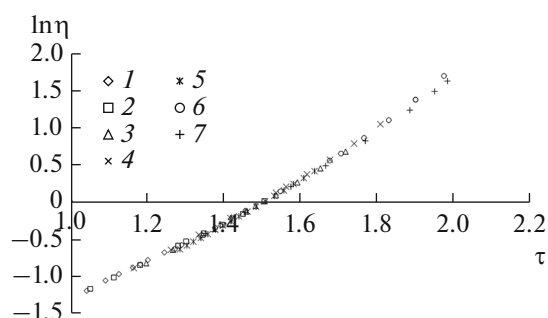
The $\ln \eta = f(\tau)$ dependence for the investigated 1-chloro-alkanes ($C_nH_{n+1}Cl$): (*1*) n = 4, (*2*) 5, (*3*) 7, (*4*) 8, (*5*) 9, (*6*) 10, (*7*) 14.

Table 2. Normal boiling temperatures of 1-chloroalkanes ($C_nH_{n+1}Cl$) and polynomial (5) coefficients

n	T_b, K [22]	n	T_b, K [22]
1	248.9	11	518.5
2	285.4	12	536.5
3	319.4	13	550.1
4	351.5	14	570.4
5	380.9	15	580.9
6	408.7	16	594.9
7	433.8	17	608.4
8	456.9	18	620.9
9	478.5	19	634.1
10	499.0	20	646.2
A_0	A_1	A_2	A_3
−2.72042	1.02444	0.32237	0.14370

viscosity logarithm will be a function of the value $\tau = T_b/T$:

$$\ln \eta = f(T_b/T).$$

The T_b value is an individual substance characteristic; for the studied liquids, we choose their normal boiling temperature. This is closely related to the critical temperature of the substance.

As it follows from the figure, the experimental $\ln \eta$ values are grouped near the common curve, thus indicating the unified activation mechanism of the temperature dependence of the liquid viscosity.

The equation for the 1-chloroalkanes of this common curve is approximated by the cubic polynomial

$$\ln \eta = A_0 + A_1\tau + A_2\tau^2 + A_3\tau^3. \qquad (5)$$

Its coefficients are given in Table 2. They make it possible to essentially extend the homolog totality and the temperature interval of the viscosity values of the liquid 1-chloroalkanes. As an example, Table 3 presents the prospected, by means of (5), viscosity values for the three homologs: 1-chloropentane, 1-chloro-decane, and 1-chlorotetradecane.

In is evident that a more exact description of the temperature dependence of the viscosity should account for the sizes of the homolog molecules.

CONCLUSIONS

Analysis of experimental data on the viscosity of 1-chloroalkanes indicates the presence of a unified activation mechanism in viscous friction related to the destruction of dimeric [19] complexes.

Table 3. Comparison of the prospected values of dynamic viscosity with experimental results

T, K	1-chloropentane			1-chlorodecane			1-chlorotetradecane		
	(5)	(2)	[15]	(5)	(2)	[15]	(5)	(2)	[15]
288.15	1.044	1.040	1.0209	2.153	2.160	2.1332	5.394	5.189	5.0257
293.15	0.968	0.966	0.9465	1.947	1.951	1.9266	4.721	4.521	4.3798
298.15	0.900	0.901	0.8818	1.770	1.772	1.7051	4.160	3.975	3.8378
303.15	0.841	0.843	0.8268	1.616	1.619	1.6015	3.690	3.524	3.4299
308.15	0.788	0.791	0.7703	1.483	1.486	1.4654	3.293	3.147	3.0634
313.15	0.740	0.744	0.7236	1.366	1.370	1.3506	2.955	2.829	2.7565
318.15	0.698	0.702	0.6807	1.263	1.268	1.2480	2.666	2.559	2.4907
323.15	0.659	0.664	0.6423	1.173	1.178	1.1574	2.417	2.327	2.2623
328.15	0.624	0.629	0.6063	1.092	1.098	1.0772	2.201	2.126	2.0687
333.15	0.593	0.597	0.5737	1.020	1.027	1.0068	2.013	1.952	1.8969
338.15	0.564	0.567	0.5441	0.956	0.963	0.9400	1.849	1.800	1.7444
343.15	0.538	0.540	0.5162	0.898	0.905	0.8832	1.704	1.666	1.6128
348.15	0.514	0.515	0.4925	0.846	0.853	0.8314	1.577	1.547	1.4997
353.15	0.492	0.492	0.4683	0.799	0.805	0.7842	1.463	1.441	1.3944

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