Relative Permittivity for 1-Chlorohexane, 1-Iodohexane, 1-Iodoheptane, and 1-Chlorononane from (293.15 to 373.15) K and Hexane + 1-Chlorohexane from (293.15 to 333.15) K

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New experimental data on relative permittivity at a frequency of 1 MHz for liquid 1-chlorohexane, 1-iodohexane, 1-iodoheptane, and 1-chlorononane from (293.15 to 373.15) K and a binary mixture of hexane + 1-chlorohexane from (293.15 to 333.15) K are reported. The uncertainty in the measured relative permittivity was ±0.1%.

Introduction

The relative permittivity provides useful information on the intermolecular interactions in liquids. As a part of our experimental program on the measurements of thermodynamic properties of haloalkanes and their mixtures,[1−3] we present here the relative permittivity of liquid 1-chlorohexane, 1-iodohexane, 1-iodoheptane, and 1-chlorononane from (293.15 to 373.15) K and hexane + 1-chlorohexane from (293.15 to 333.15) K over a mol fraction range. A literature search indicated the availability of only fragmentary dielectric properties data on the 1-chlorohexane, 1-iodohexane, and 1-iodoheptane.[4] The data on the relative permittivity of the binary mixture hexane + 1-chlorohexane are available only at 298.15 K.[5] In addition, measurements in ref 6 were carried out at 3 MHz.

Experimental Section

Materials. The materials used in this study, 1-chlorohexane, 1-iodohexane and hexane (mol fraction > 0.99), 1-iodoheptane, and 1-chlorononane (mol fraction > 0.98) were supplied from Sigma-Aldrich Ltd. All chemicals were used after purification by fractional distillation. All samples were partially degassed and dried over Fluka-type 0.4-nm molecular sieves. The purity of the products was checked by gas chromatography (GC). We obtained GC purity data of (99.3, 99.4, 98.8, 98.4, and 99.7) mol % for 1-chlorohexane, 1-iodohexane, 1-iodoheptane, 1-chlorononane, and hexane, respectively. The mixtures were prepared by mass, with a precision of $\pm 5 \times 10^{-5}$ g. The uncertainty in the mol fraction is less than 1×10^{-4}. All molar quantities are based on the IUPAC relative atomic mass table (IUPAC, 1986).[6] Experimental data of relative permittivity for 1-chlorohexane, 1-iodohexane, 1-iodoheptane, and 1-chlorononane, at various temperatures, are compared with values available in the literature and presented in Table 1.

Measurements. The relative permittivity measurements were carried out at 1 MHz, with an uncertainty of ±0.1%, using an experimental technique constructed by authors. Experimental equipment consisted of a stainless steel autoclave in which the measuring cell was located. The measuring cell was locating in the liquid. It consisted of the variable nickel capacitor brought into rotation by the electromotor DM-0.1A. The capacity of the variable capacitor was measured by an alternating current bridge E7-12 (Russia), a digital device for measurements of inductance, capacity, and resistance.

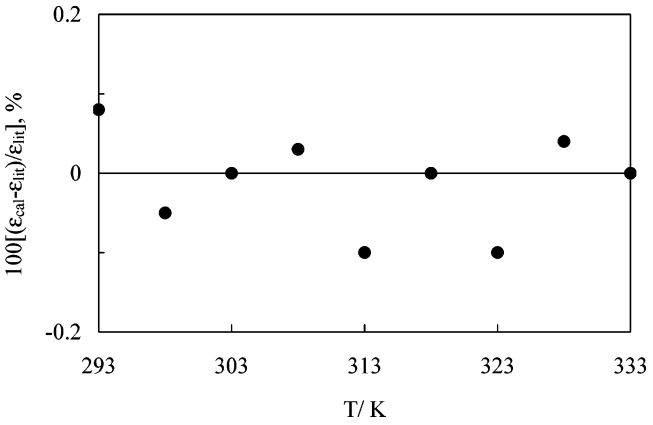

Figure 1. Deviation of our data for relative permittivity ϵ as a function of temperature from (293.15 to 333.15) K from data in ref 7. ●, our data.

Table 1. Comparison of Relative Permittivity Liquid 1-Chlorohexane, 1-Iodohexane, and 1-Iodoheptane at Different Temperatures

		ϵ	
liquid	*T*/K	this work	lit
hexane	298.15	1.884	1.89[8]
1-chlorohexane	298.15	5.853	5.821[4]
1-iodohexane	293.15	5.425	5.366[4]
1-iodoheptane	293.15	5.065	4.969[4]

The relative permittivity cell was thermostated with a temperature stability of ±0.01 K. The temperature was measured by a platinum-resistance thermometer with an uncertainty of ±0.05 K. The thermometer was placed inside the autoclave where the investigations were performed.

The technique of measurement of relative permittivity consisted of the measurement of the difference between maximal and minimal capacities of the variable capacitor in the reference and studied liquids at the set temperature. The relative permittivities ϵ were calculated by using the following relation

$$\epsilon = \frac{\Delta C}{\Delta C_0}\epsilon_0 \qquad (1)$$

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Table 2. Measured Liquid Relative Permittivity ϵ of Hexane from (293.15 to 333.15) K and 1-Chlorohexane, 1-Iodohexane, 1-Iodoheptane, and 1-Chlorononane from (293.15 to 373.15) K

	ϵ				
T/K	hexane	1-chlorohexane	1-iodohexane	1-iodoheptane	1-chlorononane
293.15	1.891	5.955	5.425	5.065	4.220
298.15	1.884	5.853	5.348	4.991	4.159
303.15	1.877	5.754	5.272	4.921	4.100
308.15	1.870	5.656	5.199	4.852	4.042
313.15	1.862	5.561	5.127	4.787	3.986
318.15	1.855	5.467	5.058	4.723	3.931
323.15	1.847	5.376	4.990	4.663	3.878
328.15	1.839	5.286	4.925	4.604	3.826
333.15	1.831	5.199	4.861	4.549	3.776
338.15		5.113	4.800	4.495	3.727
343.15		5.030	4.740	4.445	3.680
348.15		4.948	4.683	4.396	3.634
353.15		4.869	4.627	4.351	3.590
358.15		4.791	4.574	4.307	3.547
363.15		4.716	4.522	4.267	3.506
368.15		4.642	4.473	4.228	3.466
373.15		4.571	4.425	4.193	3.428

Table 3. Values of the Parameters A_j of Equation 2 and Standard Deviations for Hexane from (293.15 to 333.15) K and 1-Chlorohexane, 1-Iodohexane, 1-Iodoheptane, and 1-Chlorononane from (293.15 to 373.15) K

liquid	A_0	A_1	A_2	σ
hexane	2.0157	5.04×10^{-4}	-3.18×10^{-6}	0.001
1-chlorohexane	15.408	-4.39×10^{-2}	4.01×10^{-5}	0.002
1-iodohexane	13.458	-3.91×10^{-2}	3.99×10^{-5}	0.002
1-iodoheptane	13.739	-4.43×10^{-2}	5.01×10^{-5}	0.001
1-chlorononane	10.407	-2.99×10^{-2}	3.00×10^{-5}	0.001

where ϵ_0, ΔC, and ΔC_0 are the relative permittivities of the reference liquid, the difference between the maximal and minimal capacity of the capacitor in the studied liquid, and the reference liquid, respectively. In this method, it is not to take into account stray capacitance and to determine the geometrical sizes of the capacitor. High-purity benzene, heptane, and carbon tetrachloride were used as the reference liquids at the working temperatures. We have compared our results for the relative permittivity of the octane with the data reported in work.[7] As shown in Figure 1, it was found that our data maximum deviated by ±0.1% from the values calculated from equation $\epsilon = 1.949 \times (1-71 \times 10^{-5}(T - 293.15))$ presented in ref 7, where T is the absolute temperature.

Results and Discussion

The experimental data of relative permittivity ϵ obtained from the measurements for hexane, 1-chlorohexane, 1-iodohexane, 1-iodoheptane, and 1-chlorononane are presented in Table 2. The relative permittivity values were regressed by the method of least squares using the polynomial

$$\epsilon = A_0 + A_1 T + A_2 T^2 \qquad (2)$$

Here T is absolute temperature and A_0, A_1, and A_2 are adjustable parameters. The coefficients A_i are presented in Table 3 along with the standard deviation σ, defined by

$$\sigma = [\sum_{i=1}^{n} (\epsilon_{obs} - \epsilon_{cal})^2/(n - p)]^{1/2} \qquad (3)$$

where ϵ_{obs} and ϵ_{cal} are the observed and calculated quantities as defined earlier, n is total number of experimental points, and p is the number of parameters. The temperature dependencies of relative permittivity values ϵ for 1-chlorohexane, 1-iodohexane, 1-iodoheptane, and 1-chlorononane are also graphically presented in Figure 2.

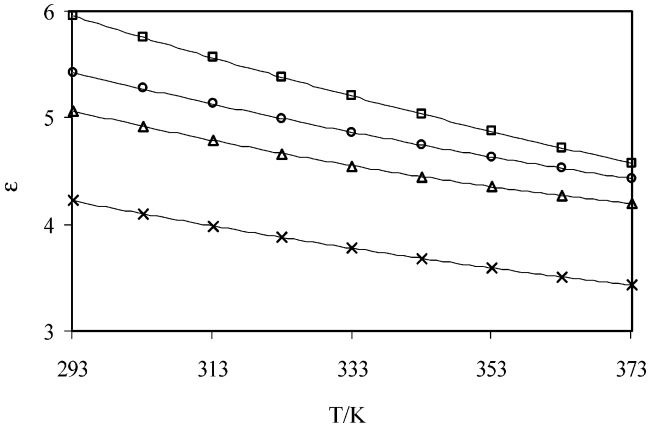

Figure 2. Relative permittivity ϵ as a function of temperature from (293.15 to 373.15) K. ×, 1-Chlorononane; □, 1-chlorohexane; △, 1-iodoheptane; ○, 1-iodohexane.

Table 4. Relative Permittivity ϵ of Hexane (1) + 1-Chlorohexane (2) from (293.15 to 333.15) K

	x_2						
T/K	0.100	0.150	0.200	0.300	0.500	0.700	0.900
293.15	2.313	2.516	2.718	3.120	3.918	4.720	5.541
298.15	2.297	2.495	2.692	3.085	3.864	4.648	5.449
303.15	2.280	2.475	2.668	3.051	3.813	4.579	5.360
308.15	2.264	2.454	2.643	3.018	3.765	4.513	5.274
313.15	2.248	2.434	2.619	2.987	3.719	4.451	5.192
318.15	2.232	2.414	2.595	2.956	3.675	4.392	5.111
323.15	2.216	2.395	2.573	2.928	3.634	4.336	5.034
328.15	2.200	2.375	2.550	2.899	3.595	4.284	4.961
333.15	2.185	2.356	2.528	2.873	3.559	4.235	4.890

The relative permittivity over the whole composition range of the binary mixtures hexane + 1-chlorohexane are given in Table 4, respectively, from (293.15 to 333.15) K. Our results for the relative permittivity for the mixture at 298.15 K are compared with the data reported in ref 6.

Our measurement results ϵ and data ϵ_{lit} presented in ref 6 at 298.15 K have been processed by polynomials of third degree in the form

$$\epsilon(x) = 0.30944x^3 - 0.44502x^2 + 4.10400x + 1.88685$$

$$\epsilon^*(x) = -1.04794x^3 + 1.73403x^2 + 3.24113x + 1.86935$$

where x is the mol composition of 1-chlorohexane. The

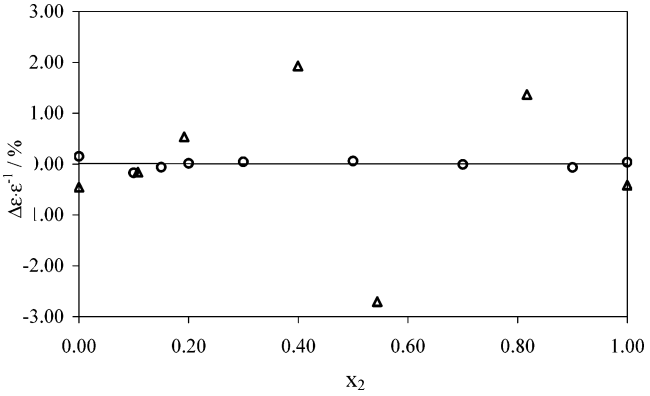

Figure 3. The relative deviations, $(\Delta\epsilon/\epsilon)$/%, from smoothed curves for hexane (1) + 1-chlorohexane (2) at 298.15 K. ○, this work; △, ref 6.

Table 5. Values Deviation in Molar Dielectric Susceptibility ($\Delta\chi/\chi$)/% of Hexane (1) + 1-Chlorohexane (2) from (293.15 to 333.15) K

	x_2						
T/K	0.100	0.150	0.200	0.300	0.500	0.700	0.900
293.15	0.32	0.75	1.27	1.65	1.92	1.59	0.48
298.15	0.22	0.68	1.20	1.57	1.87	1.56	0.49
303.15	0.21	0.57	1.04	1.49	1.77	1.49	0.48
308.15	0.15	0.53	0.95	1.36	1.57	1.35	0.43
313.15	0.03	0.39	0.79	1.14	1.33	1.14	0.33
318.15	−0.06	0.26	0.62	0.87	0.94	0.75	0.12
323.15	−0.11	0.14	0.44	0.62	0.67	0.53	0.09
328.15	−0.20	0.03	0.27	0.35	0.22	0.09	−0.14
333.15	−0.35	−0.12	0.06	−0.05	−0.00	−0.40	−0.38

deviations ϵ are from smoothed curves summarized in Figure 3. As shown in Figure 3, the presented data for pure liquids are correlated well (in the order of 0.5%). However, for mixtures in the composition region x_2 near 0.5, the presented data are significantly different from each other. As can be seen from Figure 3, our measurement results may have the deviations of 0.1% from the smoothed $\epsilon(x)$ curve that agree with uncertainty of our measurements. The values ϵ_{lit} of ref 6 are disagreed with $\epsilon^*(x)$ curve on 2% and more. Near composition $x \approx 0.5$, the deviations from $\epsilon^*(x)$ curve are maximal and change sign $((\epsilon^* - \epsilon_{lit}/\epsilon_{lit}) = +1.9\%$ at $x = 0.3996$ and $(\epsilon^* - \epsilon_{lit})/\epsilon_{lit} = -2.7\%$ at $x = 0.5441$). It may indicate that the values x presented in ref 6 are characterized by big uncertainties.

The data of the relative permittivity and density were used for the calculation of the molar dielectric susceptibility χ of mixture and pure liquids

$$\chi = \frac{(\epsilon - 1)}{4\pi}\frac{M}{\rho} \tag{4}$$

The relative deviations in the molar dielectric susceptibility $\Delta\chi/\chi$ are calculated by using the equation

$$\frac{\Delta\chi}{\chi} = \left(1 - \frac{x_1\chi_1 + x_2\chi_2}{\chi}\right) \tag{5}$$

Here x_1 and x_2 are the mol fractions of components 1 and 2, χ is the molar dielectric susceptibility of the mixture, and χ_1 and χ_2 are the molar dielectric susceptibilities of components 1 and 2, respectively. The calculated values $\Delta\chi/\chi$ are summarized in Table 5. Results of calculation χ and $\Delta\chi/\chi$ by eqs 4 and 5 are presented in Figures 4−6. As can be seen from Figures 4 and 5, the χ values are observed linear dependents of the reciprocal of the temperature $(1/T)$ for studied liquids. This clearly demonstrates the

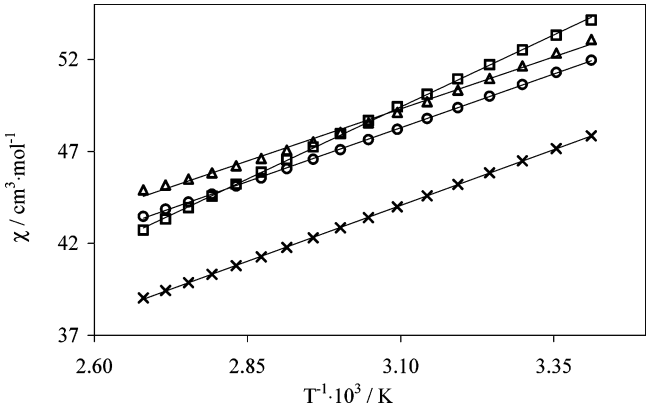

Figure 4. The molar dielectric susceptibility, χ, as a function reciprocal of the temperature $(1/T)$ for measured haloalkanes. ×, 1-chlorononane; □, 1-chlorohexane; △, 1-iodoheptane; ○, 1-iodohexane.

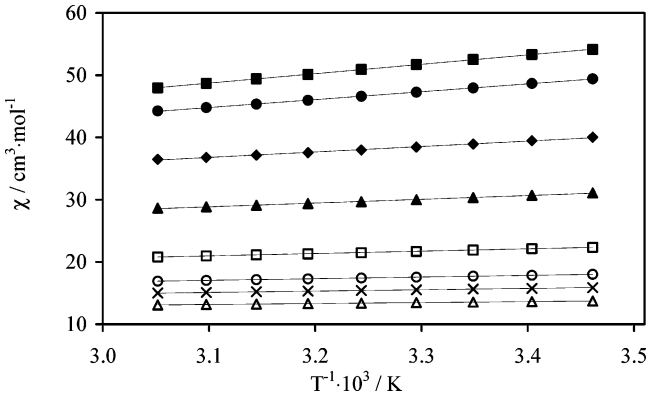

Figure 5. The molar dielectric susceptibility, χ, of hexane (1) + 1-chlorohexane (2) as a function reciprocal of the temperature $(1/T)$ (mol fraction x_2). ■, 1; ●, 0.9; ◆, 0.7; ▲, 0.5; □, 0.3; ○, 0.2; ×, 0.15; △, 0.

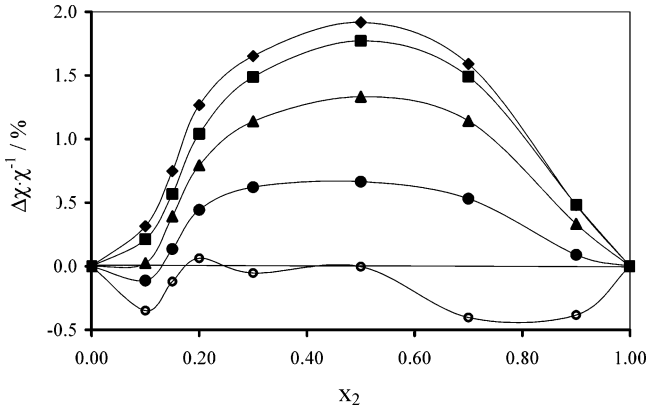

Figure 6. The relative deviation of molar dielectric susceptibility, $(\Delta\chi/\chi)$/ %, for hexane (1) + 1-chlorohexane (2). ◆, 293.15 K; ■, 303.15 K; ▲, 313.15 K; ●, 323.15 K; ○, 333.15 K.

presence of the orientational mechanism of polarization. As shown from Figure 6, the values of relative deviations $\Delta\chi/\chi$ decreases with increasing temperature. The values $\Delta\chi/\chi$ at 333.15 K change its sign.

The data of measurements values ϵ and ρ were also used for estimating the values of dipole moments of studied haloalkanes. The dipole-moment values of studied compounds obtained with the help of Onsager−Kirkwood−Frohlich's equation at $g = 1$ most closely correspond to experimental data

Table 6. Calculated Values of the Dipole Moments μ/D for Measured Haloalkanes from (293.15 to 333.15) K

T/K	1-chlorohexane	1-iodohexane	1-iodoheptane	1-chlorononane
293.15	1.94	1.75	1.75	1.71
298.15	1.95	1.75	1.76	1.72
303.15	1.95	1.76	1.76	1.72
308.15	1.95	1.76	1.76	1.72
313.15	1.96	1.77	1.77	1.72
318.15	1.96	1.77	1.77	1.72
323.15	1.96	1.78	1.77	1.72
328.15	1.96	1.78	1.78	1.72
333.15	1.96	1.78	1.78	1.72
338.15	1.97	1.79	1.79	1.72
343.15	1.97	1.79	1.79	1.72
348.15	1.97	1.80	1.80	1.73
353.15	1.97	1.80	1.80	1.73
358.15	1.97	1.81	1.81	1.73
363.15	1.97	1.81	1.82	1.73
368.15	1.97	1.82	1.83	1.73
373.15	1.98	1.83	1.83	1.73

$$\mu^2 = g\,\frac{9kT}{4\pi}\,\frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)M}{\epsilon(\epsilon_\infty + 2)^2 \rho N_A} \tag{6}$$

where M, ρ, N_A, k, μ, T, ϵ, and ϵ_∞ are the molecular weight, mass density, Avogadro's constant, Boltzmann's constant, dipole moment, absolute temperature, relative permittivity at 1 MHz, and relative permittivity characteristic of electronic polarization of haloalkanes ($\epsilon_\infty = n_D^2$), respectively. The values n_D at 293.15 K for haloalkanes are equal[9] to 1.4199 for 1-chlorohexane, 1.4929 for 1-iodohexane, 1.4904 for 1-iodoheptane, and 1.4340 for 1-chlorononane. The values n_D at other temperatures were calculated on the basis the molar refractivity, defined by the Lorentz−Lorentz's equation

$$R_m = \frac{{n_D}^2 - 1}{{n_D}^2 + 2}\,\frac{M}{\rho} \tag{7}$$

The values of the dipole moments for measured haloalkanes from (293.15 to 373.15) K calculated by eq 7 are presented in Table 6. As the data Table 6 suggest, the values of dipole moments minor increase with an increase in temperature. Their values are correlated well with experimental values presented in the handbook (1.94 D for 1-chlorohexane at 293.15 K, 1.84 D for 1-iodohexane at 298.15 K, 1.89 D for 1-iodoheptane at 293.15 K, and 1.84 D for 1-chlorononane at 295.15 K).[10]

The values of dipole moments were obtained with the help of Debye's equation

$$\frac{\epsilon - 1}{\epsilon + 2}\,\frac{M}{\rho} = \frac{4\pi N_A}{3}\left(a + \frac{\mu^2}{3kT}\right) \tag{8}$$

were more then 2 times less than the experimental values. The obtained results indicate that for the studied liquids Onsager−Frohlich's model sufficiently well simulated the local field acting on the "point" dipoles.

Literature Cited

(1) Bolotnikov, M. F.; Neruchev, Yu. A. Speed of Sound of Hexane + 1-Chlorohexane, Hexane + 1-Iodohexane, and 1-Chlorohexane + 1-Iodohexane at Saturation Condition. *J. Chem. Eng. Data* **2003**, *48*, 411−415.

(2) Bolotnikov, M. F.; Neruchev, Yu. A. Viscosities and Densities of Binary Mixtures of Hexane with 1-Chlorohexane Between 293.15 K and 333.15 K. *J. Chem. Eng. Data* **2003**, *48*, 739−741.

(3) Bolotnikov, M. F.; Neruchev, Yu. A. Temperature Dependence of the Thermophysical Properties of 1-Chlorohexane, 1-Iodohexane, 1-Iodoheptane, and 1-Chlorononane at Saturation Condition. *J. Chem. Eng. Data* **2004**, *49*, 202−207.

(4) Akhadov, Ya. Yu. *Dielectric Properties of Pure Liquids*; Izdatel'stvo standartov: Moscow, 1972.

(5) Akhadov, Ya. Yu. *Dielectric Properties of Binary Mixtures*; Nauka: Moscow, 1977.

(6) IUPAC Commission on Atomic Weights and Isotopic Abundances, 1985. *Pure Appl. Chem.* **1986**, *58*, 1677−1692.

(7) Potapov, A. A.; Lyubavina, O. I.; Podsosonnaya, O. V.; Sokova, V. V. *Tables of Standard Reference Data 24−81. Pentane, Hexane, Heptane, Octane, Nonane, Benzene, Carbon Sulfide, Carbon Tetrachloride, Cyclohexane. Dielectric Constant and Its Temperature Coefficient at Frequencies from 0.1 to 10^{11} Hz and Temperatures from 273 to 333 K*; Izdatel'stvo standartov: Moscow, 1982.

(8) Gyan, P. Johari. Dielectric Constants, Densities, and Viscosities of Acetone−1-Propanol and Acetone−*n*-Hexane Mixtures at 25 °C. *J. Chem. Eng. Data* **1968**, *13*, 541−543.

(9) Potekhin, A. A. *Properties of Organic Compounds*; Khimiya: Leningrad, 1984.

(10) Minkin, V.; Osipov, A. *The Handbook of Dipole Moments*; Vysshaya Shkola: Moscow, 1971.

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