

EXPERIMENTAL INVESTIGATION OF THE DENSITY AND VISCOSITY OF
HIGH-TEMPERATURE ORGANIC AND SILICONE HEAT-TRANSFER AGENTS IN
THE TEMPERATURE RANGE OF THEIR PRACTICAL APPLICATION

A. V. Chechetkin, V. S. Zayarnyi,* UDC 655.521.5:[532.13/14+536.22+536.63]0.8
L. A. Kreichirzhikova, and D. I. Kharaz

The densities and viscosities of several high-temperature organic and silicone heat-transfer agents are determined experimentally in the entire temperature range of their practical application under conditions of the complete absence of thermal decomposition.

The report is devoted to an experimental study of the temperature dependence and viscosity of high-temperature organic heat-transfer agents (HOHTA) and domestic silicone heat-transfer agents (DSHTA). The densities of these heat-transfer agents were measured on a Bowring installation [1]. The maximum error did not exceed $\pm 0.3\%$. And the viscosities were measured on the viscosimeter of Golubev [2], equipped for work on liquids. The maximum relative error did not exceed 2%.

Among the high-temperature heat-transfer agents presently being used in the USSR we investigated the following: a diphenyl mixture (DPM), consisting of a eutectic mixture of diphenyl and diphenyl oxide; ditolyl methane (DTM); AMT-300T aromatized oil and PMS-50 polymethyl siloxane [3]. Of those produced by the Tekhenergokhimprom PO, the Mendeleev Moscow Chemical and Technological Institute, and the Institute of Organic Chemistry, Academy of Sciences of the USSR, we investigated the following heat-transfer agents: the terphenyl mixture 10ZK, consisting of diphenyl, o-terphenyl, m-terphenyl, and phenanthrene, diphenyldixylene hydroxysilane (DPDXHS), IS-20 and IS-45 oil heat-transfer agents, the combination heat-transfer agent KT-1, consisting of DPM and MIPT (monoisopropyl terphenyl), the combination heat-transfer agents KT-2 and KT-3, consisting of DPM and DTM, and the combination heat-transfer agent KT-4, consisting of DPDXHS and the terphenyl mixture 10ZK [3-5].

The experimental data were treated on a MIR-2 computer.

For all the heat-transfer agents studied we found the temperature dependence of the density in the form

$$\rho = A - Bt - Ct^2. \quad (1)$$

In Table 1 we give the values of the constants A, B, and C in Eq. (1), the temperature range in which the densities were measured, and the values of the relative approximation error R and the rms error L.

The noneutectic mixtures, which the combination heat-transfer agents KT-2, KT-3, and KT-4 are, were tested for additivity through the equation

$$\rho = g_1\rho_1 + g_2\rho_2. \quad (2)$$

The results of the corresponding calculations are presented in Table 2, from which it follows that under the conditions of the complete absence of thermal decomposition of the components of combination heat-transfer agents their density obeys the additivity rule.

For all the investigated heat-transfer agents the temperature dependence of the dynamic viscosity was found in the form

$$\mu = A_0 \exp \frac{B}{T}, \quad (3)$$

$$\mu = \frac{A}{(t + \alpha)^n}. \quad (4)$$

*Deceased.

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TABLE 1. Values of the Constants A, B, and C in Eq. (1)

Heat-transfer agent index	A	B	C · 10 ⁵	Rel. approx. error R, %	Rms. error L	Range of temp. t, °C
10ZK	1102,28	0,842	-0,189	0,116	0,4	20-400
DPM	1069,66	0,6797	49,6	1,33	0,3	20-400
DTM	996,8	0,7947	20,4	0,56	1,66	20-380
DPDXHS	1109,4	0,7593	0,215	0,013	0,045	20-240
PMS-50	975,4	0,8397	-0,408	0,17	0,94	20-330
KT-1	1116,1	1,3307	-195	0,33	2,12	20-360
KT-2	1030,1	0,8386	-23	0,27	1,26	20-370
KT-3	1048,7	0,7557	21,3	0,13	0,64	20-350
KT-4	1103,3	0,7784	-12,1	0,41	1,7	20-330
AMT-300T	1003,0	-0,0177	580	1,20	5,94	20-300
IS-20	892,3	0,6452	11,35	0,21	0,71	20-300
IS-45	929,7	0,6633	-6,48	0,26	0,74	20-300

TABLE 2. Disagreement between Test Values of ρ and Values Calculated from Eq. (2)

Heat-transfer agent index	Values of $(\rho_t - \rho_c)/\rho_t$, %, at temps. of					
	20	100	200	300	350	380
KT-2	-0,66	-0,52	+0,22	-2,09	+3,73	+5,69
KT-3	-0,22	+0,22	+0,19	+0,42	+0,45	-2,09
KT-4	-0,42	-0,38	-1,04	-1,89	-	-

TABLE 3. Values of Constants A₀ and B in Eq. (3)

Heat-transfer agent index	A ₀ · 10 ⁵	B	Rel. approx. error R, %	Rms error L	$(\mu_t - \mu_c)/\mu_t$ %, at 100°C	Range of temp. t, °C
10ZK	1,60	1772,0	2,3	0,06	-4,2	90-400
DPM	0,93	1801,0	1,8	0,095	+15,5	20-350
DTM	0,91	1742,6	5,96	0,16	-9,2	20-380
DPDXHS	280,3	920,9	3,3	0,046	-3,0	60-240
PMS-50	8,70	1864,2	1,0	0,035	+0,7	60-330
KT-1	0,75	2091,1	10,7	0,15	-17,2	20-360
KT-2	1,13	1686,2	4,6	0,075	-10,3	20-370
KT-3	1,70	1378,2	3,0	0,074	-11,5	20-250
KT-4	22,9	1574,4	8,6	0,12	+15,7	60-330
AMT-300T	7,95	1791,6	12,4	0,16	-17,2	50-290
IS-20	2,3	2031,3	3,8	0,08	-4,4	90-300
IS-45	15,4	1564,3	5,7	0,13	-12,8	90-300

TABLE 4. Values of Constants A, α , and n in Eq. (4)

Heat-transfer agent index	A	α	n	Rel. approx. error R, %	Rms error L	$(\mu_t - \mu_c)/\mu_t$ %, at 100°C
10ZK	54,99	60,0	2,03	2,46	0,069	+4,8
DPM	5,00	35,0	1,72	1,39	0,062	+7,5
DTM	4,86	40,0	1,74	3,50	0,160	-9,2
DPDXHS	1,47	6,0	0,81	1,21	0,031	+4,8
PMS-50	52,19	20,0	1,74	2,13	0,055	+3,4
KT-1	47,96	37,0	2,059	5,90	0,087	+9,5
KT-2	3,421	37,5	1,658	1,98	0,029	+3,7
KT-3	0,394	36,0	1,30	3,02	0,076	+9,5
KT-4	17,27	10,0	1,50	3,50	0,110	+1,7
AMT-300T	243,44	50,0	2,02	10,8	0,140	-23,0
IS-20	252,5	45,0	2,16	3,08	0,072	+5,6
IS-45	41,65	45,0	1,67	5,00	0,120	+15,5

In Table 3 we present the values of the constants A₀ and B in Eq. (3), the temperature range in which the densities were measured, the values of the relative approximation error R and the rms error L, and the departure of the calculated values of μ from the test values.

TABLE 5. Values of Relative Difference between Test Values of Viscosity and Those Calculated from Eqs. (5), (6), and (7)

Heat-transfer agent index	Calc. from Eq.	Values of $(\mu_t - \mu_c)/\mu_t$, % at t, °C				
		20	100	200	300	350
KT-2	(5)	-8,9	+3,66	+2,8	+0,88	-1,9
	(6)	-9,4	+12	+1,98	+0,44	-2,0
	(7)	-9,4	+2,3	+1,98	0,0	-0,56
KT-4	(5)	+29*	-37	-43	-102*	-140‡
	(6)	+53†	-7,2	-10	-18†	-30,5‡
	(7)	+49‡	+18	-40	-78†	-102‡

*At 60°C. †At 260°C. ‡At 330°C.

In Table 4 we present A, α , and n in Eq. (4), the values of the relative approximation error R and the rms error L, and the departure of the calculated values of μ from the test values.

It follows from an analysis of Tables 3 and 4 that the test data on the viscosity of one- and two-component heat-transfer agents agree better with Eq. (4) than with (3). The test data on the viscosity of multicomponent heat-transfer agents (the terphenyl mixture 10ZK, the aromatized oil AMT-300T, and the oil heat-transfer agents IS-20 and IS-45) agree with both equations in equal measure.

Of the combination heat-transfer agents, KT-2 represents a mixture of HOHTA which belongs to the third group of high-temperature heat-transfer agents. KT-4 consists of an HOHTA and a DSHTA, i.e., it is a mixture of heat-transfer agents of the third and second groups [3]. In this connection it is interesting to check on the additivity of KT-2 and KT-4. For them we calculated the values of the viscosity through the viscosities of the components of these mixtures through the Arrhenius equations [6],

$$\lg \mu_{\text{mix}} = g_1 \lg \mu_1 + g_2 \lg \mu_2, \quad (5)$$

$$\lg \mu_{\text{mix}} = x_1 \lg \mu_1 + x_2 \lg \mu_2 \quad (6)$$

and from the equation of Kendall and Monroe [6],

$$\mu_{\text{mix}}^{1/3} = x_1 \mu_1^{1/3} + x_2 \mu_2^{1/3}. \quad (7)$$

The results of these calculations are presented in Table 5 in the form $(\mu_t - \mu_c)/\mu_t$, the relative difference between the test values of the viscosity and those calculated from the equations given above. It is seen from the table that the viscosity of a heat-transfer agent consisting of an HOHTA and a DSHTA (the heat-transfer agent KT-4) does not obey the additivity rule. For KT-2 the best agreement with the additivity rule is observed when the viscosity is calculated from the equation of Kendall and Monroe [6]. The heat-transfer agent KT-2 represents a mixture of HOHTA only.

NOTATION

ρ , ρ_1 , ρ_2 , densities of heat-transfer agent and of its components, respectively, kg/m^3 ; μ , μ_1 , μ_2 , coefficients of dynamic viscosity of heat-transfer agent and of its components, $\text{N}\cdot\text{sec/m}^2$; T, t, temperature, °K and °C, respectively; g_1 , g_2 , mass fractions of components of combination heat-transfer agent; x_1 , x_2 , molar fractions of components of combination heat-transfer agent. Indices: t, test value; c, calculated value.

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DENSITY MEASUREMENT IN LIQUID H₂-D₂ SOLUTIONS

Yu. A. Milenko and R. M. Sibileva

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Molar and excess molar volumes of liquid H₂-D₂ solutions are determined by dielectric constant measurements.

Because of quantum effects, the thermodynamic properties of the condensed phases of hydrogen isotopes differ markedly from each other, and their solutions are nonideal, being characterized by excess quantities, in particular, an excess molar volume:

$$V^E = V(p, T) - [V_1(p, T)c_1 + V_2(p, T)c_2], \quad (1)$$

where V is the molar volume of the mixture at a given pressure T and pressure p ; $V_{1,2}$, molar volumes of the pure components under the same conditions; and $c_{1,2}$, component molar concentrations in the solution.

The excess molar volumes of H₂-D₂ solutions at temperatures $T \leq 20.4^\circ\text{K}$ have been measured previously in [1-3]. The results of those studies show that $V^E < 0$, agree qualitatively with each other, but show large quantitative differences.

In the present study molar volumes of H₂-D₂ solutions were determined by measuring the dielectric constant ϵ . This method requires knowledge of the polarization (Clausius-Mossotti function) P of the pure materials and the concentration dependence of P for the mixture. The polarization of H₂ and D₂ for $T \leq 20.4^\circ\text{K}$ has been determined previously [4,5]. The function $P(c)$ was assumed linear.

The resonant frequency ($\sim 10^{10}$ Hz) of an empty and completely filled resonator was measured to determine ϵ .

This method and experimental technique have been used previously to measure ϵ in mixtures of *o*- and *p*-hydrogen, and *o*- and *p*-deuterium [4,5].

The experimental uncertainties were: in frequency, ± 0.2 MHz, which corresponds to an ϵ uncertainty of $\pm 0.8 \cdot 10^{-4}$; in temperature (parahydrogen condensation thermometer) $\pm 0.01^\circ\text{K}$ ($\Delta\epsilon \approx 4 \cdot 10^{-5}$). Data on *p*-H₂ saturation pressure were taken from [6].

The mixtures were prepared at room temperature, measuring the partial pressures of the pure components and using the equation of state of an ideal gas. Practically no change in liquid concentration due to liquid-vapor separation occurred, since the quantity of vapor phase was negligibly small. The uncertainty in concentration determination was 0.15% ($\Delta\epsilon = \pm 0.8 \cdot 10^{-4}$). The total uncertainty in ϵ determination was not more than $\pm 2 \cdot 10^{-4}$.

Equilibrium with respect to *o*-*p* composition at 20.4°K of the H₂ and D₂ (*p*-H₂ and *e*-D₂) was obtained by maintenance in an Fe(OH)₃ catalyst. Room temperature equilibrium H₂ and D₂ (*n*-H₂ and *n*-D₂) were prepared by holding the gas in a glass tube in the presence of an incandescent platinum filament. It should be noted that this method cannot produce normalization of previously prepared H₂-D₂ mixtures, since the HD formation reaction occurs intensely under these conditions.

Dielectric constants of liquid H₂-D₂ solutions with the following compositions were measured: 30.2, 49.6, 69.9 mol. % D₂ for mixtures of *n*-H₂-*n*-D₂, and 29.9, 49.9, 69.7 mol. % D₂ for *p*-H₂-*e*-D₂ mixtures along the liquid-vapor equilibrium line at temperatures from the

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