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THERMAL CONDUCTIVITY OF METHANOL–N OCTANOL BINARY SOLUTIONS AT DIFFERENT TEMPERATURES AND PRESSURES

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Results of investigation into the thermal conductivity of methanol–N octanol solutions at different temperatures, pressures, and concentrations are presented.

One of the most important physicochemical characteristics of binary solutions of aliphatic alcohols is the thermal-conductivity coefficient λ, which is undoubtedly of great interest. In view of the fact that there is no information on reliable theoretical and empirical methods for calculating this coefficient, it is of prime importance to determine it experimentally.

The present work is devoted to experimental investigation into the thermal conductivity of liquid binary solutions of methyl and N octyl alcohols at pressures of 0.101–60 MPa, temperatures of 290–600 K, and concentrations of 0.25, 0.50, and 0.75 in weight fractions.

We carried out the experiments on a modified installation by the regular-regime method [1–3]. The same installation was employed previously to determine the thermal conductivity of pure N octyl alcohol [4]; on this installation, we also performed a control measurement of λ for methyl alcohol as a model liquid [1]. Comparison of the newly obtained data on λ of methyl alcohol and the existing data [5] showed their satisfactory agreement. The present investigation extends information on λ of the methanol–N octanol system, which makes it possible to obtain the interrelations of λ for binary solutions. We must point out the fact that the data on λ of both pure components and their mixtures were obtained on similar installations, and this circumstance makes it possible to exclude systematic errors having the same directions and values in experiments and to establish a more exact concentration dependence of the thermal conductivity of the solutions in processing the results obtained.

For investigations we used pure methyl and N octyl alcohols. The solutions under study are prepared by the gravimetric method on a VLA-200g-M analytical balance with the observance of the required accuracy.

The thermal conductivity of the methanol–N octanol solutions was measured with a temperature step of about 25 K and a pressure step of 5 and 10 MPa.

The error of the results obtained for the thermal conductivity of the solutions was determined according to the general theory of errors [6] and was equal to $\pm 1.8\%$.

The calculated heat-conduction equation is similar to that given in [2, 7] with certain correction terms. In the experiments, we measured the rate of cooling. Knowing the geometrical dimensions of the measuring cell and the characteristics of the kernel, we calculated the thermal-conductivity coefficient of the solution from the existing formula [2]. For the first time, the experimental data on the thermal conductivity of methanol–N octanol solutions at different temperatures and pressures are obtained. The results of the experiments are presented in Table 1. As an example, we showed the dependences of the thermal conductivity of the solutions on the concentration of methanol at a pressure of 50 MPa by isotherms (Fig. 1a) and at a temperature of 460 K by isobars (Fig. 1b).

From the analysis of the results obtained in determining λ of the methanol–N octanol system (see Table 1 and Fig. 1) it is evident that the concentration dependence of the mixtures deviates from the additivity line in the negative direction and is symmetric relative to the concentration of the constituent components of the mixture. It should be noted that in [8] the deviation ($\delta\lambda$) has the same direction at atmospheric pressure. However, the influence of the temperature is different. An increase in the pressure and temperature favors a decrease in the deviation. Thus, for example, in the case of a concentration of $(50 + 50)\%$, whereas at P = 0.1 MPa and T = 293 K we have $\delta\lambda = \lambda_{ad} - \lambda_{0.5} =$

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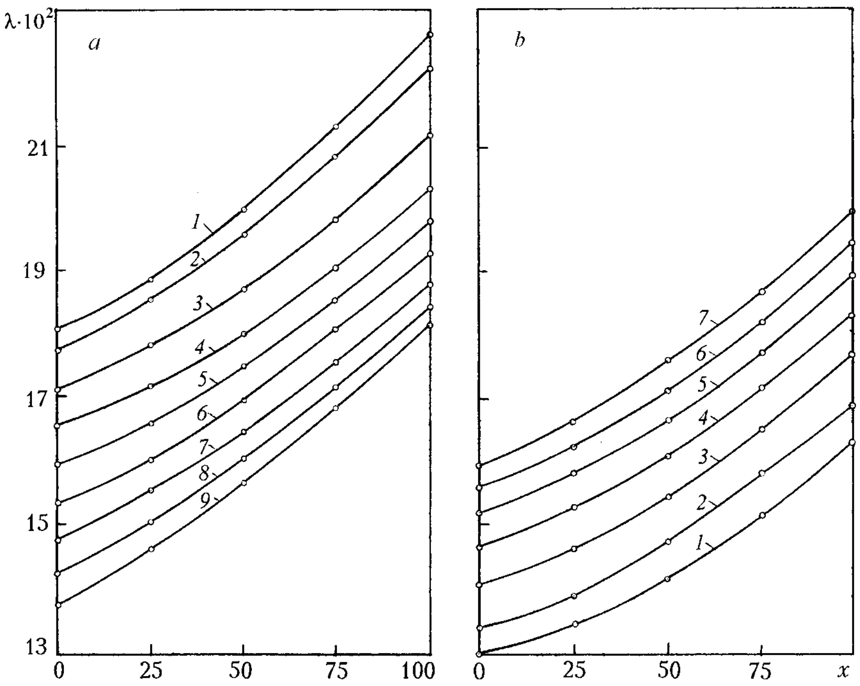

Fig. 1. Dependence of the thermal conductivity of the liquid binary methanol-N octanol solutions on the methanol concentration at 50 MPa and different temperatures (a), at 460 K and different pressures (b): a) 1) 300 K; 2) 320; 3) 360; 4) 400; 5) 440; 6) 480; 7) 520; 8) 560; 9) 600; b) 1) 5 MPa; 2) 10; 3) 20; 4) 30; 5) 40; 6) 50; 7) 60.

$56 \cdot 10^{-4}$ W/(m·K) and $\delta\lambda/\lambda_{0.5} = 3.2\%$; then already at $P = 10$ MPa and $T = 500$ K we have $\delta\lambda = 42 \cdot 10^{-4}$ and $\delta\lambda/\lambda_{0.5} = 3.0\%$, and at $P = 60$ MPa and $T = 293$ K we have $\delta\lambda = 43 \cdot 10^{-4}$ and $\delta\lambda/\lambda_{0.5} = 2.1\%$.

A similar situation is also observed for concentrations of $(25 + 75)\%$ and $(75 + 25)\%$.

The data on λ as a function of P, T, and x obtained for each of the investigated solutions are described by a concentration equation of the form

$$\lambda = \lambda_1 x_1 + \lambda_2 x_2 + 10^{-4} x_1 x_2 (\alpha \Delta T + \beta P - \gamma) . \tag{1}$$

The values of the coefficients entering into Eq. (1) are found from the experimental data and are equal to $\alpha = 0.2286$, $\beta = 0.8667$, and $\gamma = 241.46$. The maximum error throughout the investigated interval amounts to $\pm 0.8\%$.

Generalization of the experimental data on the thermal conductivity of methanol–N octanol solutions and their components is worthy of note. In [9], to describe the dependence of the thermal conductivity of organic liquids on the temperature and pressure, use was made of the modified Tate equation

$$\lambda_P = \lambda_0 + A(T) \ln \frac{B(T) + P}{B(T) + P_0} . \tag{2}$$

To determine the coefficients $A(T)$ and $B(T)$ in Eq. (2), we applied the procedure proposed in [10], whose essence lies in determining the coefficient B by simultaneous solution of two isothermal Tate equations in integral form written for different pressures along one isotherm:

$$\frac{\lambda_{P_1} - \lambda_0}{\lambda_{P_2} - \lambda_0} = \frac{\ln [(B + P_1)/(B + P_0)]}{\ln [(B + P_2)/(B + P_0)]} . \tag{3}$$

Hence it is possible to find the coefficient B and then the coefficient A from Eq. (2).

TABLE 1. Experimental Values of the Thermal Conductivity ($\lambda \cdot 10^4$, W/(m·K)) for Methanol and N Octanol Solutions at Different Pressures and Temperatures

T, K	P, MPa								
	0.101	1	5	10	20	30	40	50	60
25% methanol + 75% N octanol									
291.3	1666	1673	1700	1731	1783	1825	1864	1901	1937
319.7	1597	1605	1631	1664	1723	1769	1808	1848	1887
345.3	1537	1546	1572	1609	1671	1720	1761	1803	1841
370.7	1483	1492	1519	1558	1622	1675	1719	1760	1800
400.6	1420	1429	1457	1500	1565	1623	1671	1714	1752
421.2		1383	1420	1464	1532	1592	1642	1684	1723
445.8		1334	1374	1422	1493	1553	1607	1650	1688
470.4			1328	1379	1453	1516	1574	1616	1655
496.5			1275	1325	1409	1479	1538	1584	1624
520.0			1207	1266	1368	1443	1506	1554	1598
545.5				1188	1320	1405	1472	1523	1571
574.7				1100	1258	1364	1434	1493	1540
601.0				1050	1206	1325	1404	1464	1515
50% methanol + 50% N octanol									
290.7	1765	1772	1800	1832	1886	1931	1973	2010	2050
318.4	1691	1699	1726	1760	1819	1868	1908	1950	1993
343.8	1627	1636	1663	1700	1762	1813	1855	1899	1942
368.6	1565	1574	1601	1642	1703	1758	1804	1847	1890
390.2		1532	1559	1603	1664	1721	1770	1814	1856
417.6		1467	1504	1552	1617	1678	1729	1773	1816
444.4			1455	1504	1575	1638	1693	1737	1782
471.3			1395	1453	1530	1598	1657	1703	1748
495.6			1336	1398	1489	1561	1625	1676	1721
519.4				1318	1443	1523	1594	1647	1697
542.3				1218	1395	1486	1563	1621	1675
572.6				1085	1310	1442	1527	1594	1648
600.9				1025	1240	1398	1497	1568	1625
75% methanol + 25% N octanol									
291.7	1886	1893	1922	1956	2012	2058	2101	2140	2182
319.2	1807	1816	1842	1878	1937	1985	2026	2070	2115
344.7	1738	1746	1774	1811	1873	1921	1967	2013	2057
370.8		1683	1711	1753	1813	1865	1911	1955	2000
395.6		1620	1655	1699	1756	1815	1864	1910	1954
420.0			1600	1651	1716	1777	1828	1872	1919
446.1			1557	1610	1681	1743	1798	1844	1892
471.7			1487	1553	1630	1700	1759	1810	1858
499.2			1396	1474	1580	1657	1723	1777	1828
525.1				1360	1523	1610	1690	1748	1804
548.8				1212	1457	1570	1658	1725	1783
574.2				1082	1371	1532	1630	1705	1765
601.2				1018	1290	1489	1604	1685	1748

TABLE 2. Values of the Coefficients a_i and b_i in Eqs. (4) for the System (50 + 50)% Methanol–N Octanol

i	a_i	b_i
0	0.2266333	440.2383284
1	–0.000728284	–1.482827
2	0.0000007	0.00129381

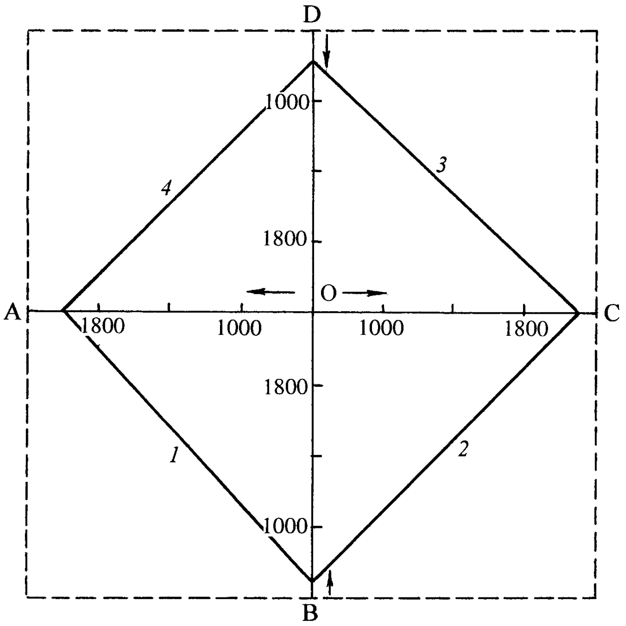

Fig. 2. Interrelations of the thermal conductivities of the systems methanol–N hexanol, methanol–N heptanol, methanol–N octanol, and methanol–N nonanol with a 50% concentration of methanol: 1) for the solutions (OA–BO); 2) (BO–OC); 3) (OC–DO); 4) (DO–OA), where O is methanol, A is N hexanol, B is N heptanol, C is N octanol, and D is N nonanol.

The coefficient B for a $(50 + 50)\%$ methanol–N octanol system was numerically determined on a computer using the "half-division" method. The dependences of A and B on the temperature were approximated in the form of the polynomials

$$A = \sum_{i=0}^{n=2} a_i T^i , \quad B = \sum_{i=0}^{m=2} b_i T^i . \tag{4}$$

The values of a_i and b_i are given in Table 2. The maximum error of Eqs. (2)–(4) amounts to 1.0%.

In [11], to generalize the experimental data on the thermal conductivity of the solutions it was suggested to use a closed three-coordinate system. However, this procedure allows one to generalize the data on only three solutions (of different concentrations or different composition) at once. Here, the three-axis coordinate system is unsuitable for four solutions simultaneously. Thus, it is necessary to use a four-axis coordinate system. In the present work, we make an attempt to apply such a system to four different solutions. The use of the four-axis coordinate system will make it possible to relate the thermal conductivities of the solutions by a simple dependence, to generalize them graphically and predict the thermal conductivities of the solution studied with the use of the other three solutions, and to perform, if necessary, interpolation and extrapolation. The essence of the method is presented below.

The thermal conductivities of the systems methanol–N hexanol, methanol–N heptanol, methanol–N octanol, and methanol–N nonanol investigated previously and in the present work are generalized on a four-coordinate system (OA, BO, OC, and DO) (Fig. 2); the values of the thermal conductivity of one indicated solution (methanol with the higher alcohol) are plotted on each coordinate axis. As an example, we take $(50 + 50)\%$ solutions of the indicated alcohols. For the sake of simplicity, the scales of thermal conductivity are assumed to be the same. The horizontal coordinates OA and OC start from the central point O, while the vertical coordinates BO and DO, on the contrary, start from the points B and D in the direction of the point O. Using perpendicular grids at prescribed P and T we find the points of intersection of the thermal conductivities of the solutions. The pairs of the solutions give the curves inside the four-axis coordinate system. Since here there are four combinations of pairs, we obtain curves 1–4, which form a quadrangle. The generalization has shown that these curves are depicted with an accuracy of 3.1% by straight lines of the form $\lambda' = m\lambda'' + n$. As a result, this equation takes the following specific forms:

$$\lambda_2' = 1.148\lambda_1' - 238.35\,, \quad \lambda_3' = 0.9155\lambda_2' + 177.46\,, \quad \lambda_4' = 1.019\lambda_3' - 40.20\,, \quad \lambda_1' = 0.934\lambda_4' + 76.15\,. \tag{5}$$

Equations (5) allow determination of the thermal conductivity of a given solution using the other three solutions, which is very important for a mutual check of the calculation accuracy.

NOTATION

λ, thermal-conductivity coefficient, W/(m·K); λ_1 and λ_2, thermal conductivities of the first and second components; $\delta\lambda$, deviation from the additivity rule; $\lambda_{\rm ad}$, value of the thermal conductivity of the solutions on the additivity line; $\lambda_{0.5}$, value of the thermal conductivity of the solutions at $x_1 = x_2 = 0.5$; P, pressure, MPa; T, temperature, K; x_1 and x_2, concentrations of the first and second components, weight fractions; $\Delta T = T - T_0$; T_0, base temperature, $T_0 = (T'_{\rm ml} + T''_{\rm ml})/2$; $T'_{\rm ml}$ and $T''_{\rm ml}$, melting temperatures of the first and second components, K; α, β, and γ, constant coefficients of Eq. (1) for the given system; λ_0 and λ_P, thermal conductivities of the liquid on the saturation line and at the pressure P, W/(m·K); P_0, atmospheric pressure or saturation pressure; $A(T)$ and $B(T)$, temperature-dependent coefficients; λ_{P_1} and λ_{P_2}, thermal conductivities at the isotherm temperature and at the pressures P_1 and P_2; λ' and λ'', thermal conductivities of the studied and the known systems; m and n, constants for the considered pair of systems; λ_1', λ_2', λ_3', and λ_4', thermal conductivities of the first (methanol–N hexanol), second (methanol–N heptanol), third (methanol–N octanol), and fourth (methanol–N nonanol) solutions. Subscripts: ad, additivity; ml, melting.

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