Journal of Engineering Physics and Thermophysics, Vol. 76, No. 2, 2003

INVESTIGATION OF THE HEAT CONDUCTIVITY OF MUTUAL SOLUTIONS OF METHYL AND ISOPROPYL ALCOHOLS AT VARIOUS TEMPERATURES AND PRESSURES

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UDC 536.223

The results of an experimental study of the dependence of the heat conductivity of binary solutions of methyl and isopropyl alcohols on the concentration, temperature, and pressure are presented. An empirical equation for calculating this index is proposed.

The extensive use of aliphatic alcohols in various chemical productions and in many fields of engineering calls for detailed investigations of their thermophysical and thermodynamic properties. Analysis of the literature sources has shown that for a number of aliphatic alcohols the heat conductivity has been studied in a wide range of state parameters [1]. At the present time, however, information about it for mutual solutions of alcohols is actually absent. This induced the authors to study in detail the heat conductivity of binary solutions of methanol with some normal alcohols and isoalcohol.

The heat conductivity of methanol at high pressures was investigated in [2–5] and that of isopropanol — in [2, 6–8]. Comprehensive analysis and comparison of the results of the above publications have shown that to establish the concentration dependence of the heat conductivity of the methanol–isopropanol system, one can successfully use, besides the experimental data obtained by us as reference data, the information for pure methanol from [3, 5] and for pure isopropanol from [6, 7]. This also follows from the fact that the authors of both [3, 6] and the present paper used the regular regime method having in both cases equal systematic errors (1.3%), which were mutually eliminated when the concentration dependence of λ was established.

In the present paper, an experimental study of the heat conductivity of methanol (CH_3OH)–isopropanol (CH_3H_7OH) solutions has been made for mass concentrations of 25, 50, and 75% in the 0.1–50 MPa range of pressures and the 293–500 K range of temperatures.

The investigated alcohols had the following characteristics: methanol — refractive index n_D^{20} = 1.3288, density ρ_4^{20} = 791.15 kg/m^3, melting temperature T_{melt} = 175.49 K, boiling temperature T_{boil} = 337.70 K, critical temperature T_{cr} = 512.64 K, and critical pressure P_{cr} = 8.096 MPa; isopropanol — n_D^{20} = 1.3773, ρ_4^{20} = 785.2 kg/m^3, T_{melt} = 184.68 K, T_{boil} = 355.39 K, T_{cr} = 508.30 K, and P_{cr} = 4.762 MPa.

The experiments were performed by the regular regime method on the set developed by us [9]. Its basic component is a high-pressure tricalorimeter designed to measure the heat conductivity of electrolytes. The design and the principle of operation of the calorimeter are described in [5, 9]. Preliminarily, on the set control measurements of the heat conductivity of model liquids (*n*-heptane and methanol) were made. The results of the experiments were compared with the most reliable literature data. The maximum discrepancy was 2%.

A number of refinements taking into account heat losses in the measuring cells were introduced into the heat-conduction equation [9]. We made no correction for the heat radiation, since alcohols are strongly absorbing liquids. Neither did we make a correction for the heat loss from the ends of the measuring cylinder, since, according to the principle of operation of the new tricalorimeter, it is excluded in the process of heat-conductivity measurement and does not enter into the heat calculation equation.

The absence of convection in the layer of the liquid under investigation is confirmed in experiments by the equal values of the heat conductivity under the same conditions but at different temperature differences between the internal and external cylinders as well as by the fact that the Ra criterion in all cases did not exceed 600.

Azerbaijan Technical University, Baku. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 76, No. 2, pp. 177–181, March–April, 2003. Original article submitted June 25, 2002.

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TABLE 1. Experimental Values of the Heat Conductivity ($\lambda \cdot 10^4$, W/(m·K) of Methanol–Isopropanol Solutions

T, K	P, MPa							
	0.1013	1	5	10	20	30	40	50
25 mass % of methanol + 75 mass % of isopropanol								
292.5	1475	1479	1501	1527	1579	1626	1671	1715
311.7	1434	1439	1461	1487	1538	1590	1636	1682
336.6	1386	1393	1414	1440	1494	1546	1594	1642
364.8		1341	1365	1395	1449	1502	1550	1598
385.1		1303	1329	1363	1420	1472	1521	1569
407.6		1266	1293	1331	1389	1444	1495	1544
435.9			1252	1293	1356	1413	1465	1517
460.0			1213	1261	1331	1389	1446	1501
483.7			1162	1221	1303	1366	1426	1484
505.4				1174	1276	1345	1410	1470
50 mass % of methanol + 50 mass % of isopropanol								
291.9	1600	1605	1632	1661	1718	1769	1817	1864
315.5	1544	1552	1575	1606	1665	1717	1767	1815
338.1	1493	1502	1527	1559	1619	1673	1724	1774
366.2		1445	1473	1506	1567	1622	1674	1724
388.4		1401	1431	1468	1529	1587	1639	1690
409.8		1360	1394	1435	1497	1559	1613	1665
436.2			1350	1398	1466	1527	1585	1640
459.7			1309	1364	1440	1503	1565	1621
484.3			1249	1317	1407	1477	1542	1604
508.6				1267	1379	1456	1526	1588
75 mass % of methanol + 25 mass % of isopropanol								
292.6	1786	1791	1821	1853	1912	1964	2010	2055
313.5	1728	1736	1763	1795	1856	1907	1955	2004
334.9	1673	1681	1708	1742	1805	1856	1905	1955
360.0		1623	1652	1688	1749	1804	1855	1904
387.3		1561	1593	1633	1693	1749	1802	1853
408.6		1519	1554	1598	1660	1720	1775	1826
439.4			1490	1544	1615	1678	1735	1789
460.2			1448	1508	1587	1651	1713	1768
482.7			1382	1462	1550	1624	1690	1748
507.5				1380	1506	1590	1665	1727

In the experiments, the temperature was measured by a standard PTS-10 resistance thermometer with an error of ±0.5 K. The pressure in the experiments was created and measured simultaneously by an MP-600 dead-weight pressure-gauge tester of accuracy class 0.05.

The solutions for the investigations were prepared in a quartz vessel by the gravimetric method on a VLA-200-g-M analytical balance. Chemically pure alcohols were used.

The basic dimensions of the tricalorimeter measuring cell are as follows: the external diameter of the internal measuring cylinder is 12.255 mm, the internal diameter of the external cylinder is 12.931 mm, the value of the annular gap is 0.338 mm, the measuring cylinder length is 140 mm, and the length of the compensation cylinders is 40 mm.

The experiments were performed on isothermic lines with a temperature step of ~25 K. The results are presented in Table 1 for rounded values of pressure. The reproducibility of results is ~0.3%. The top value of temperature in experiments was limited to ~510 K for fear of the appearance of thermodiffusion in the solution layer in the vicinity of the pseudocritical point (T_{pcr} = 510.47 K at $x_1 = x_2 = 0.5$).

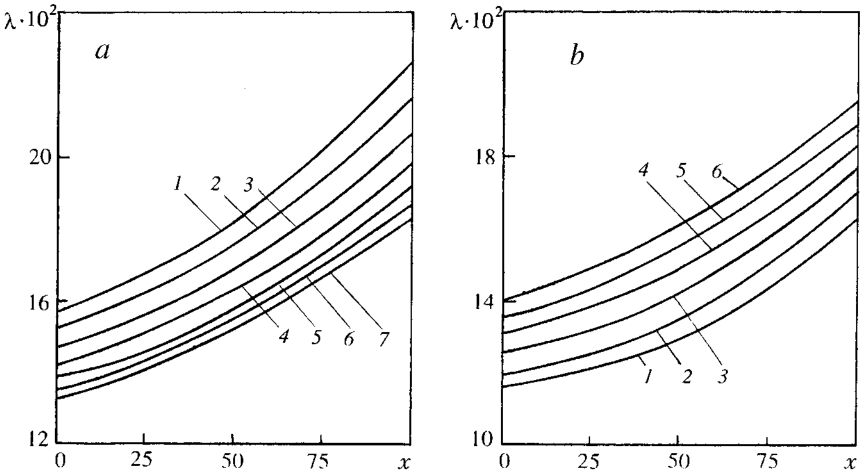

Fig. 1. Heat conductivities of liquid binary methanol–propanol solutions as a function of the methanol concentration: (a) at a pressure of 40 MPa and various temperatures: 1) T = 293; 2) 320; 3) 360; 4) 400; 5) 440; 6) 480; 7) 500 K; (b) at a temperature of 460 K and various pressures: 1) P = 5; 2) 10; 3) 20; 4) 30; 5) 40; 6) 50 MPa. λ, W/(m·K); x, mass %.

Figure 1a shows the concentration dependence of the heat conductivity of the methanol–isopropanol solutions at 40 MPa and various temperatures, and Fig. 1b — the same, at 460 K and various pressures. From Table 1 and Fig. 1 it is seen that the heat conductivity of the investigated solutions does not obey the additivity law and deviates from it towards negative values for the region of state parameters (the concentration curves are arranged symmetrically about the straight lines of additivity). In this case, the value of $\delta\lambda$ depends not only on the concentration of components but also on the temperature and pressure (as the latter increase, it decreases). A similar picture was also observed for other systems of aliphatic alcohols (normal and isoalcohols). Comparison of the concentration dependence of the heat conductivity of the systems methanol–normal alcohols and methanol–isoalcohols shows that it is much stronger for the latter (by about 20%).

Detailed analysis of the experimental data obtained allows us to propose the following empirical equation:

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

where $\Delta T = T - T_0$; $T_0 = (T'_{\mathrm{melt}} + T''_{\mathrm{melt}})/2$.

For the investigated methanol–isopropanol system we have obtained: $\alpha = 0.7428$, $\beta = 3.067$, and $\gamma = 592.2431$. The error of equation (1) does not exceed the experimental one.

To generalize the experimental data on the heat conductivity of liquids and gases at high pressures, one may successfully use the Vargaftik dependence [10] relating the excess heat conductivity to the density:

$$\lambda - \lambda_0 = f(\rho) \,. \tag{2}$$

The chief disadvantage of expression (2) is the fact that it includes the density, which itself is thought of as a quantity to be determined and is a function of temperature and pressure. In using formula (2), it is necessary to predetermine the density, since for many solutions it is not known.

Works [11, 12] give an equation of state of matter well defining experimental density data (with a maximum error of 0.1%):

$$f(\rho) = A_0 (T) + B_0 (T)\, P^{0.5} + C_0 (T)\, P \,. \tag{3}$$

Combining (2) and (3), we can obtain a simple heat-conduction equation in the form

$$(\lambda - \lambda_0)^2 = A (T) + B (T)\, P^{0.5} + C (T)\, P \,. \tag{4}$$

TABLE 2. Values of Coefficients a_i, b_i, and c_i in Eq. (4)

i	a_i	b_i	c_i
0	0.03024315344	$0.86937003 \cdot 10^{-2}$	$-0.288886 \cdot 10^{-3}$
1	$0.438077528 \cdot 10^{-4}$	$-0.6898569246 \cdot 10^{-4}$	$0.24853091 \cdot 10^{-5}$
2	$-0.3591977 \cdot 10^{-6}$	$0.17768172 \cdot 10^{-6}$	$-0.6577933 \cdot 10^{-8}$
3	$0.336487445 \cdot 10^{-9}$	$-0.146694972 \cdot 10^{-9}$	$0.558719 \cdot 10^{-11}$

TABLE 3. Comparison of the Experimental and Calculated (by Eq. (4)) Heat Conductivities for the 50% Methanol + 50% Propanol Solution

T, K	λ_0, W/(m·K)	P, MPa								
		5			20			40		
		I	II	ε	I	II	ε	I	II	ε
300	159	1610	1616	0.40	1699	1703	0.24	1800	1808	0.45
340	193	1523	1519	0.30	1615	1605	0.62	1720	1710	0.60
380	236	1445	1447	0.14	1543	1542	0.07	1651	1649	0.12
420	283	1375	1382	0.51	1486	1499	0.90	1602	1615	0.82
460	333	1308	1307	0.10	1439	1446	0.50	1564	1566	0.13
480	358	1260	1261	0.10	1413	1413	0	1546	1543	0.20
500	384				1384	1381	0.22	1529	1534	0.33

Note: I) experiment; II) calculation; $\varepsilon = (\lambda_{calc} - \lambda_{exp}) \cdot 100/\lambda_{exp}$, %.

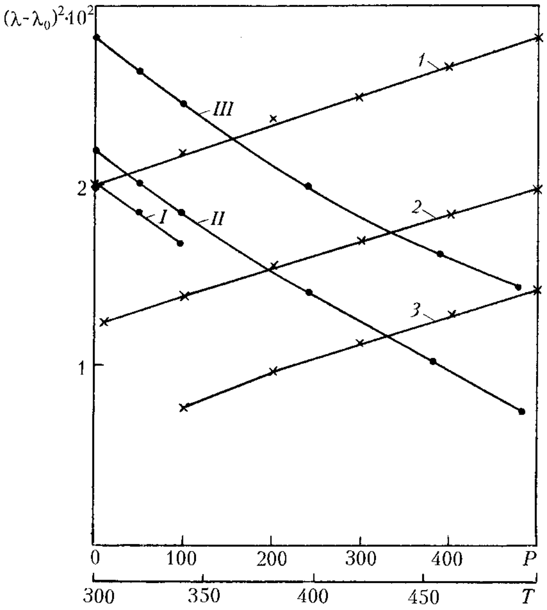

Fig. 2. Excess heat conductivity of the 50% methanol + 50% propanol solution as a function of pressure and temperature: 1) 300; 2) 400; 3) 500 K; I) 1 bar; II) 100; III) 500 bars. $(\lambda - \lambda_0)^2$, $(\mathrm{W/(m \cdot K)})^2$; P, bar; T, K.

For approximate calculations, we have

$$(\lambda - \lambda_0)^2 = A'(T) + C'(T)\,P\,. \tag{5}$$

In Eqs. (4) and (5), P is determined in bars.

The constants $A(T)$, $B(T)$, $C(T)$, $A'(T)$, and $C'(T)$ are found from the experimental data. It should be noted that the value of λ_0 for solutions can be found from the additivity law, since for the gas phase the deviation of the heat conductivity from the additivity line is insignificant. Moreover, always $\lambda_0 < \lambda$. Thus, Eq. (4) can be used successfully for solutions.

The use of dependences (4) and (5) for methanol and isopropanol and their solutions has shown that both equations are convenient for practical use, but (4) is more exact and convenient, although it contains more coefficients.

The values of the coefficients of Eq. (4) were found on a computer by the least-squares method and are given in Table 2:

$$A = \sum_{i=0}^{3} a_i T^i \,, \; B = \sum_{i=0}^{3} b_i T^i \,, \; C = \sum_{i=0}^{3} c_i T^i \,. \tag{6}$$

We have used Eq. (4) to generalize the data on λ of a 50% methanol + 50% isopropanol solution. Table 3 compares smoothed experimental and calculated values of the heat conductivities of the solution. The results of the comparison are quite satisfactory. The maximum discrepancy is 0.9% at T = 420 K and P = 20 MPa.

The dependence of the excess heat conductivity of the solution of 50% methanol + 50% isopropanol is shown in Fig. 2, from which it is seen that the dependence $(\Delta\lambda)^2 = f(P)$ is almost rectilinear.

NOTATION

n_D^{20}, refractive index; λ, heat conductivity of liquid at various P and T, W/(m·K); λ_0, heat conductivity of gas at atmospheric pressure and at different T; λ_s, heat conductivity of solution; λ_1 and λ_2, heat conductivities of the first and second components of the solution; $\delta\lambda$, value of deviation of the experimental heat conductivity from the additive one; $\Delta\lambda = (\lambda - \lambda_0)$, excess heat conductivity (difference of the heat conductivities of liquid and gas); x_1 and x_2, concentrations of the first and second components, in fractions; P, pressure, MPa; T, temperature, K; T_0, base temperature; T'_{melt} and T''_{melt}, melting temperatures of the first and second components; Ra, Rayleigh criterion; ε, error of the calculated equation (4) compared to the experimental data; p, liquid density at various P and T, kg/m^3; α, β, γ, constants for the given system; $A_0(T)$, $B_0(T)$, $C_0(T)$, constants for determining the density; $A(T)$, $B(T)$, $C(T)$, $A'(T)$, $C'(T)$, constants for determining the excess heat conductivity. Subscripts: a, b, c, coefficients of polynomials; melt, melting; s, solution; pcr, pseudocritical; exp, experimental; boil, boiling; cr, critical; calc, calculated; i, number of polynomial members.

REFERENCES

1. Ya. M. Naziev, A. N. Shakhverdiev, N. S. Aliev, and M. M. Bashirov, *Thermal Properties of Monobasic Alcohols* (*Heat Conductivity*). *Reviews on the Thermophysical Properties of Substances* [in Russian], Moscow (1992).
2. P. Bridgman, *The Physics of High Pressures* [Russian translation], Moscow–Leningrad (1935).
3. I. F. Golubev and T. N. Vasil'kovskaya, *Teploénergetika*, No. 5, 77–81 (1969).
4. I. Kh. Mukhamedziyanov, *Experimental Study of Heat Conductivity of Liquid Organic Compounds at Pressures up to 2500 bars*, Author's Abstract of Candidate Dissertation (in Engineering), Kazan' (1972).
5. M. M. Bashirov and Ya. M. Naziev, *Probl. Énerget.*, No. 4, 133–139 (2001).
6. T. N. Vasil'kovskaya and I. F. Golubev, in: *Chemistry and Technology of Nitrogenous Fertilizers and Products of Organic Synthesis* [in Russian], Issue 23, Moscow (1969), pp. 121–135.
7. T. N. Vasil'kovskaya and I. F. Golubev, *Teploénergetika*, No. 6, 84–86 (1969).
8. H. Forsman, P. Anderson, and F. Bacstrom, *Physica*, **114B**, No. 3, 287–294 (1982).
9. Ya. M. Naziev and M. M. Bashirov, *Izv. Ross. Akad. Nauk, Énergetika*, No. 3, 157–162 (2002).
10. N. B. Vargaftik, *Heat Conductivity of Compressed Liquids and Gases*, Author's Abstract of Doctoral Dissertation (in Engineering), Moscow (1952).
11. Ya. M. Naziev and V. G. Gasanov, *Zh. Prikl. Khim.*, **68**, Issue 2, 210–213 (1995).
12. S. S. Tsimmerman and V. M. Miniovich, *Zh. Fiz. Khim.*, **51**, No. 1, 208–209 (1977).