RESEARCH THERMAL CONDUCTIVITY OF BINARY SOLUTIONS OF NORMAL ALCOHOLS AT HIGH PRESSURES

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Introduction. Binary solutions of alcohols are wide used in chemical, oilchemical and other fields of industry. In connection with this it is necessary to research their thermal properties, and also thermal conductivity (λ) at high pressure [1]. But at the present days the there isn't paid enough attention to learning thermal conductivity of reciprocal solutions of normal alcohols. That was the reason, why authors of this work began to study very detailly thermal conductivity of methanol′s binary solution with some normal alcohols. This work concerns to experimental research of thermal conductivity of liquid binary solution of methanol (CH_3OH) with 1- propanol (C_3H_7OH), 1- octanol ($C_8H_{17}OH$), 1-undecanol ($C_{11}H_{23}OH$) at mass concentration 25, 50 and 75 % at pressure range 0.1- 60 MPa and temperature range 290-600 K.

For research were used pure methyl, n.propil, n. Okthil and n.undesil alcohols. Studied solutions were prepared by fraction of total mass on analytical balance VLA-200-M with observance of required accurasy.

Experimental device. Thermal conductivity of above mentioned binary solutions was measured on the new modificated device, applied for research of electrolyte by new method cylindrical tricalorimeter of regular regime . According to new tricalorimeter′s the theory it becomes real to increase reliability of measurement λ as all experiments were carried out by the method, where the face loss of heat of measuring cylinder are excepted automatically and it isn′t included into equation. [2]. It is necessary to note that the quantity of thus loss isn't little-for calorimeters, measuring thermal conductivity of electrolyte [3] it is equal to 3-5% for liquids and to 8-10% for gas from the common quantity of heat flow.

Experimental installation mainly consist of system for creation, keeping and measurement of temperature, system for creation, keeping and measurement of pressure, of system for measurement thermal conductivity.

The main part of device is cylindrical λ-calorimeter, with construction given on fig.1. Geometric dimensions of measuring cell of calorimeter are the following: outside diameter of nucleus 1 d_1=12.255 mm; inside diameter of outside cylinder- d_2 =12.931 mm; value of ring hole 2-δ=0.338mm; inside diameter of outside cylinder 3 D=37 mm; length of inside 1 and outside 3 measuring cylinders ℓ=140 mm, length of inside 4 and outside 5 protection cylinders ℓ_0=40 mm.

After fixing of heat mode in device we make measurement of substance thermal conductivity. First of all for to get difference in temperature between autoclave 10 and outside measuring cylinder the last is allowed to cool at Δt_3=1-1,5 K by feed vapour of liquid nitrogen from Dewar flask through side tube 8, which is in outside cylinder. As a result the temperature of nucleus decreases. Then the inside heater is switched on. The temperature of nucleus monotonically rises, crosses line of autoclave temperature and rises up to 1-2 K. Then heater is switched off and nucleus in outside cylinder is allowed to cool. So the temperature of outside cylinder doesn't change or changes very little because of its large mass, in consider with nucleus mass and cool by vapour of liquid nitrogen. As a result measuring cell and nucleus characteristic we count thermal conductivity of solution by the known formula [2].

Results of experiments. For the first time we have got experimental data by λ of researched solutions at various temperatures and pressures the results of research on thermal conductivity of liquid binary solutions methanol-n.propanol, methanol-n.octanol and methanol-n.undercanol are given in table 1-3. Error of got results is determined according to common theory of error [4] and is equal to 1,8%.

On the base of the got result′s analysis by λ of system is clear, that mixture′s concentration is slopping towards negative side from the line of additivity and is symmetric about line of additivity.

It is necessary to note, that the negative deviation of thermal conductivity for solutions of normal alcohols methanol-n. hexanol and methanol-n.nonanol (at temperature at 20-80^0 C and atmospheric pressure) was determined earlier [5]. Influence of double molecules interaction on thermal conductivity of solution has the difficult nature.

Consideration of the experiment results. For to describe plot thermal conductivity of solutions as a function of pressure (P), temperature (T) and concentration of components (x) we suggest the said equation.

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

where λ_1, λ_2 - thermal conductivity of first and second components; x_1, x_2 -concentration of first and second components, in fraction of total mass; α, β, γ -constants for this system, the results are given in table 4.

$$\Delta T=T-T_0 ,$$

T_O -base temperature

$$T_O= (T'_m + T''_m)/2,$$

T'_m, T''_m - temperature of melting of first and second components.

The careful overall analysis and comparison of literature data by λ of clear alcohols showed, that for to set concentrational dependence (1) of thermal conductivity of systems methanol-n.propanol, methanol-n.octanol, methanol-n.undecanol, beside it we can use these data for pure methanol from [6,7], for n. pro-ponol from [8], for n.octanol from [9], for n.undercanol from [10]. As in work [6-10], as in present work we applied the method of regular regime, having the same systematic errors in both cases (1,3%) which are impossible at dependence λ=f(x).

Equation (1) describes experimental data by λ of binary solutions with maximal error ±1,0% in all researched interval of condition parameters.

Literature

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Table 1. Experimental data of thermal conductivity $(\lambda \cdot 10^4, W/(mK))$ of methanol and n. propanol solutions at different temperatures and pressures.

T,K	P, Мпа							
	0,1013	1	5	10	20	30	40	50
1	2	3	4	5	6	7	8	9
25% methanol +75 n. propanol								
291,3	1614	1618	1631	1661	1706	1747	1787	1827
312,5	1566	1572	1589	1617	1662	1705	1744	1784
336,7	1512	1519	1540	1567	1617	1662	1701	1741
360,1		1471	1495	1524	1576	1623	1665	1707
389,2		1416	1440	1472	1528	1578	1623	1665
416,8		1364	1393	1429	1487	1542	1588	1632
445,4			1345	1387	1449	1506	1555	1601
469,1			1303	1350	1417	1477	1528	1576
489,3			1263	1315	1389	1452	1506	1555
507,9				1275	1363	1428	1485	1535
50% methanol +50% n. propanol								
292,5	1700	1705	1724	1756	1807	1852	1895	1937
311,1	1652	1658	1679	1709	1763	1810	1850	1894
334,7	1595	1602	1625	1656	1711	1761	1801	1846
361,2		1544	1567	1602	1658	1709	1753	1798
384,3		1496	1521	1559	1616	1667	1715	1761
410,5		1441	1471	1513	1573	1629	1680	1726
439,9			1420	1466	1533	1591	1644	1693
472,6			1356	1413	1486	1549	1607	1658
503,5			1257	1339	1438	1508	1573	1627

75% methanol +25% n.propanol								
1	2	3	4	5	6	7	8	9
291,6	1844	1849	1875	1907	1962	2009	2053	2095
311,2	1789	1795	1819	1853	1909	1957	2000	2044
332,2	1733	1740	1764	1798	1856	1905	1950	1995
354,4		1684	1711	1746	1805	1856	1901	1947
380,0		1624	1652	1693	1749	1802	1849	1896
406,2		1563	1595	1639	1699	1758	1807	1856
435,7			1537	1588	1657	1716	1769	1819
461,3			1486	1545	1618	1682	1740	1790
483,5			1419	1494	1580	1651	1715	1767
506,2				1422	1539	1618	1688	1744

Table 2. Experimental data of thermal conductivity $\left(\lambda \cdot 10^4, W / (mK)\right)$ of methanol and n. octonol solutions at different temperatures and pressures.

T, K	P,Mпa								
	0,101	1	5	10	20	30	40	50	60
25% methanol+75% n.octonol									
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.octonol								
	0,101	**1**	**5**	**10**	**20**	**30**	**40**	**50**	**60**
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. octonol								
	0,101	**1**	**5**	**10**	**20**	**30**	**40**	**50**	**60**
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 3. Experimental data of thermal conductivity $(\lambda \cdot 10^4, W/(mK))$ of methanol and n. undecanol solutions at different temperatures and pressures.

T.K	P,MPa								
	0,101	1	5	10	20	30	40	50	60
<u>25%</u> methanol +75% n. undecanol									
297,7	1742	1748	1773	1805	1859	1912	1959	2002	2042
321,8	1633	1641	1668	1702	1761	1811	1861	1903	1946
346,4	1544	1553	1579	1614	1675	1724	1775	1817	1859
371,1	1471	1479	1505	1540	1602	1650	1700	1742	1785
395,4	1407	1416	1441	1478	1535	1587	1636	1678	1720
419,3	1350	1361	1385	1422	1481	1535	1583	1626	1667
444,5	1291	1300	1329	1369	1430	1485	1534	1578	1617
470,2		1240	1273	1317	1381	1438	1490	1534	1575
496,2		1183	1215	1263	1334	1394	1450	1495	1538
520,0		1118	1158	1206	1294	1357	1417	1466	1508
544,9			1055	1132	1250	1320	1383	1436	1482
570,6			968	1064	1202	1285	1353	1408	1457
599,4			930	1017	1150	1249	1323	1382	1435
	<u>50%</u> methanol +50% n. undecanol								
	0,101	1	5	10	20	30	40	50	60
297,9	1815	1822	1847	1880	1938	1988	2032	2076	2116
322,4	1716	1724	1752	1785	1845	1895	1943	1984	2031
347,1	1633	1641	1670	1705	1764	1815	1864	1906	1950
372,5	1560	1569	1598	1634	1693	1744	1793	1838	1880
399,2	1491	1500	1528	1567	1625	1680	1730	1774	1817
420,0		1446	1480	1521	1583	1640	1689	1733	1778
446,2		1385	1423	1470	1536	1593	1644	1691	1733
471,3		1310	1365	1419	1489	1550	1606	1652	1697
495,9		1230	1300	1360	1444	1510	1571	1618	1666
521,4			1194	1277	1396	1468	1536	1588	1638
546,1			1005	1165	1340	1425	1504	1562	1615
580,0			810	1041	1252	1380	1466	1532	1588
600,7				1008	1206	1352	1445	1515	1574

	75% methanol +25% n. undecanol								
	0,101	1	5	10	20	30	40	50	60
298,2	1906	1914	1939	1974	2033	2081	2125	2168	2208
320,0	1828	1835	1862	1898	1957	2005	2049	2093	2141
344,8	1748	1756	1785	1820	1881	1931	1979	2024	2070
369,1	1682	1690	1720	1755	1815	1868	1918	1960	2005
392,7		1629	1658	1699	1757	1814	1863	1905	1952
418,6		1559	1598	1644	1707	1764	1814	1857	1905
444,9		1490	1542	1593	1660	1723	1774	1821	1868
468,3		1418	1484	1546	1619	1684	1741	1789	1837
491,8		1294	1411	1485	1575	1645	1709	1760	1810
516,1			1295	1390	1524	1604	1676	1733	1786
540,0			1100	1258	1466	1562	1644	1707	1764
574,4			896	1070	1355	1507	1607	1680	1740
603,0				1008	1272	1466	1580	1660	1724

Table 4. The values of coefficients α, β, γ in equaation (1) for systems methanol -n.propanol, methanol -n. octonol, methanol - n. undecanol

Systems	α	β	γ
Methanol -n.propanol	0.443	1.667	482.641
Methanol -n. octonol	0.2286	0.8667	241.46
Methanol n. undecanol	0.1714	0.600	174.34

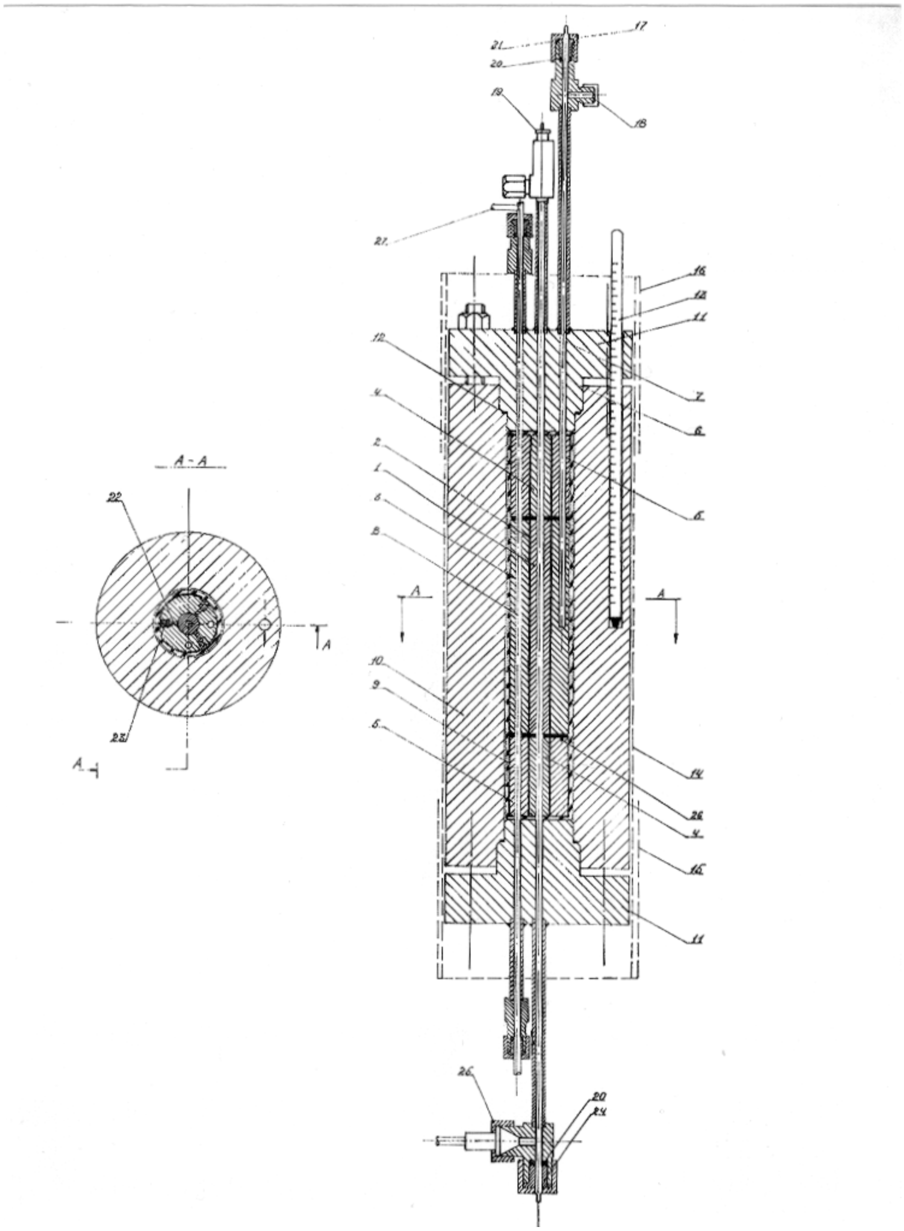

Fig.1. Device the cylindrical λ-calorimeter