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THERMAL CONDUCTIVITY OF AMYL AND ISOAMYL PROPIONATES

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Results of an experimental study of thermal conductivity of amyl and isoamyl propionate over the temperature range 300-600°K at pressures of 0.1-50 MPa are presented.

Complex ethers of propionic acid are used in the cellulose industry as high-boiling-point solvents for nitrocellulose and as plasticizers for cellulose acetate, although their transfer properties have not been studied over a wide range of state parameters.

The coaxial cylinder method with stationary regime [1] was used to study the thermal conductivity coefficient. The measurement cell consisted of two coaxially arranged cylinders of refined copper. The inner diameter of the outer cylinder was 13.13 mm, with outer diameter of 80 mm. A set of internal cylinders 140 mm long with diameters of 11.01, 12.03, and 12.40 mm was used. The thickness of the propionate layer studied was 0.55 mm in the liquid phase and 0.36 mm in the gaseous phase. Working surfaces of the cylinders were polished and chromium-plated. All other components of the device were made of type 1Kh18N9T stainless steel.

The temperature differential across the liquid layer was measured by a six-junction Chromel—Copel differential thermocouple, calibrated to a 10-Ω standard platinum resistance thermometer to an accuracy of 0.02°K. Three holes were drilled to a depth of 30, 60, and 98 mm in the outer and inner cylinders to hold the thermocouple junctions, which were held in place by copper inserts.

Use of a material with high thermal conductivity (red copper) for the measurement cylinder reduced axial temperature gradients to values less than the sensitivity of the thermocouples [2].

A heater made of 0.15-mm-diameter Constantan wire was located along the axis of the inner cylinder. The power dissipated by this heater was measured by a potentiometric circuit using the voltage drop across the heater and a 10-Ω reference winding connected in series with the heater. Temperature was measured by a 10-Ω resistance thermometer (No. 2000, constructed at VNIIFTRI). Pressure was generated and controlled by a piston manometer, type MP-600, class 0.05.

The equation used to calculate the thermal conductivity coefficient from the experimental data included all the characteristic corrections for this method [1, 3].

TABLE 1. Thermal Conductivity of Air at Atmospheric Pressure

T, °K	308,2	341,1	386,3	438,1	486,0	527,1	569,0
$\lambda\cdot 10^4$, W/m·degK	263	292	325	360	387	426	549

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TABLE 2. Thermal Conductivity λ of Heptane, W/m·deg K, at Various Temperatures and Pressures

T, °K	P, MPa						
	0,1	5,0	10	20	30	40	50
296,2	0,1285	0,1313	0,1333	—	0,1372	—	0,1398
339,7	0,1250	0,1275	0,1304	0,1337	0,1416	0,1449	0,1487
373,0	—	0,1124	0,1150	0,1203	0,1247	0,1301	0,1341
482,2	—	0,0948	0,0973	0,1053	0,1119	0,1173	0,1285

Heat loss through the cylinder end surfaces was calculated with consideration of the fact that the cell construction ensures operation of the inner cylinder end faces in the planar horizontal layer method. The value of this correction is 3.16%, and it has been included in the thermal conductivity coefficient calculation [3].

The absence of convective heat exchange with similar gap sizes in liquid and gas layers has been established by many experimental studies [4].

To verify the validity of the experimental technique, control measurements of λ were made for air at atmospheric pressure over the temperature interval 290-600°K. Reproducibility of the data was verified by measuring λ at various gap thicknesses and heater powers. The values of λ for air for one series of measurements ($\delta = 0.55$ mm) are shown in Table 1.

Measurements were also made of the thermal conductivity of n-heptane at temperatures of 296-566°K and pressures of 0.1-50 MPa. The results obtained agreed within the limits of experimental error with the data of [5, 6]. A portion of this data is presented in Table 2.

The uncertainty of the results of liquid and gas measurements by the coaxial cylinder method over the entire temperature interval studied was ±(1.4-2.7)% at a confidence level $\alpha = 0.95$ [3].

The purity of the reagents studied was not less than 99.8% by weight ("Tsvet-4" chromatograph). Measurements were performed along isotherms with steps in temperature of 25-30°K and in pressure of 5-10 MPa, over the temperature interval 300-600°K and pressure range 0.1-50 MPa. In calculating λ for the vapor, a correction was introduced for radiation

TABLE 3. Thermal Conductivity Coefficient λ of Amyl Propionate, W/m·deg K

T, °K	P, MPa						
	0,1	5	10	20	30	40	50
300	0,138	0,140	0,142	0,144	0,147	0,150	0,153
325	0,133	0,135	0,137	0,140	0,142	0,145	0,148
350	0,127	0,129	0,132	0,135	0,138	0,141	0,144
375	0,122	0,124	0,127	0,130	0,133	0,136	0,139
400	0,117	0,119	0,122	0,125	0,128	0,132	0,135
425	—	0,114	0,117	0,120	0,124	0,127	0,131
450	—	0,108	0,111	0,115	0,119	0,123	0,127
475	—	0,103	0,106	0,110	0,114	0,118	0,122
500	—	0,099	0,102	0,106	0,110	0,114	0,118
525	—	0,095	0,098	0,102	0,106	0,110	0,113
550	—	0,091	0,094	0,098	0,102	0,106	0,110
575	—	0,087	0,090	0,095	0,099	0,103	0,107

Saturation line				Vapor					
liquid		vapor		0,1 MPa		1,0 MPa		2,0 MPa	
T, °K	λ	T, °K	λ	T, °K	λ	T, °K	λ	T, °K	λ
440	0,108	460	0,0235	425	0,017	593	0,040	592	0,0425
467	0,104	470	0,025	450	0,021	604	0,042	603	0,044
480	0,100	502	0,129	475	0,025	637	0,045	628	0,0465
495	0,097	537	0,033	500	0,029	662	0,048	651	0,049
512	0,094	561	0,037	525	0,033	680	0,050	680	0,0515
526	0,091	582	0,042	550	0,038*				
560	0,085	592	0,0475	515	0,148*				

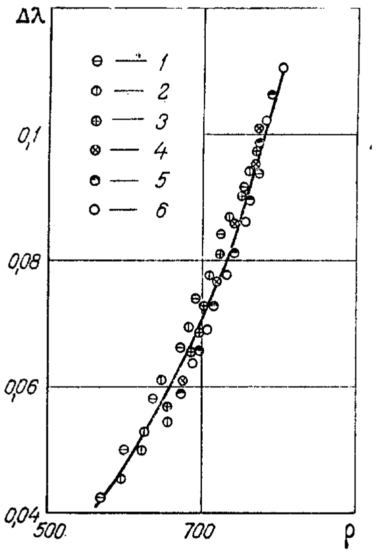

Fig. 1. Excess thermal conductivity of amyl propionate versus density at various pressures, MPa: 1) 5; 2) 10; 3) 20; 4) 30; 5) 40; 6) 50. Δλ, W/m·deg K; ρ, kg/m^3.

by the method of [7], the propionate vapor being considered as weakly absorbing the infrared radiation of the medium. Several experimental points are available for the thermal conductivity of liquid amyl propionate [5], at atmospheric pressure. Within the limits of experimental error, the present data agree with that of Mukhamedzyanov and Ustanov.

No data are available in the literature for the thermal conductivity of liquid or gaseous isoamyl propionate.

The results obtained in the present study for thermal conductivity of amyl and isoamyl propionates inliquid and gaseous phases, and also on the saturation line, are presented in Tables 3 and 4.

The thermal conductivity of the propionates in the liquid phase decreased with temperature over the entire pressure range studied. The most significant change in λ with change in

TABLE 4. Thermal Conductivity Coefficient λ of Isoamyl Propionate, W/m·deg K

T, °K	P, MPa						
	0,1	5	10	20	30	40	50
300	0,128	0,130	0,132	0,135	0,138	0,141	0,144
325	0,124	0,126	0,128	0,131	0,134	0,137	0,140
350	0,119	0,121	0,123	0,126	0,129	0,132	0,135
375	0,115	0,116	0,119	0,122	0,125	0,128	0,131
400	0,111	0,113	0,115	0,118	0,121	0,124	0,127
425	0,019	0,109	0,111	0,114	0,117	0,120	0,124
450	0,023	0,104	0,106	0,110	0,113	0,116	0,120
475	0,027	0,100	0,102	0,106	0,110	0,113	0,117
500	0,031	0,095	0,098	0,102	0,106	0,109	0,113
525	0,035	0,091	0,094	0,098	0,102	0,106	0,110
550	0,039	0,087	0,090	0,094	0,098	0,103	0,107
575	0,043	0,083	0,086	0,090	0,095	0,100	0,104
600	0,047	0,079	0,082	0,087	0,092	0,097	0,101

Saturation line				Vapor					
liquid		vapor		0,1 MPa		0,9 MPa		1,4 MPa	
T, °K	λ	T, °K	λ	T, °K	λ	T, °K	λ	T, °K	λ
446	0,103	488	0,030	425	0,019	582	0,045	590	0,0475
473	0,098	535	0,038	450	0,023	636	0,053	616	0,052
498	0,094	570	0,044	475	0,027	666	0,058	650	0,057
514	0,091	587	0,049	500	0,031	685	0,061	685	0,062
529	0,088	600	0,055	525	0,035				
549	0,084	605	0,059	550	0,039				
570	0,080			575	0,043				
588	0,077			600	0,047				

TABLE 5. Coefficients of Eq. (3) for Isoamyl Propionate

a_i	b_i
$a_0=1745,78831$ $a_1=-74159,37109$ $a_2=1041986,00781$ $a_3=-5173649,25000$	$b_0=0,62788$ $b_1=221,76283$ $b_2=-2904,14916$ $b_3=16410,54395$

temperature was found at low pressures, further increase in pressure producing a weaker temperature dependence in λ.

As can be seen from the tables, the conductivity of isoamyl propionate in the liquid phase is less than λ of amyl propionate. This is related to the fact that in iso-compounds the mean molecular distance is ≈0.38 Å larger than in normal ethers [8], which causes some decrease in the interaction energy and thermal conductivity of iso-compounds.

The thermal conductivity of the propionates in the gas phase increases linearly with temperature. At high temperatures λ of amyl propionate becomes more sensitive to temperature because of pyrolysis. At high temperatures decomposition of molecular complexes and individual molecules occurs, which is accompanied by liberation of additional thermal fluxes due to chemical reactions [9]. The region in which pyrolysis occurs is noted in Table 3 by an asterisk. No pyrolysis was observed in the isoamyl propionate λ measurements. Apparently in iso-compounds the molecular complexes and molecules are more stable with respect to decay and dissociation. Thermal conductivity of isoamyl propionate in the gaseous phase is greater than λ of normal propionate.

To verify the dependence of excess thermal conductivity upon density an experimental study of the P—V—T curves of the propionates was performed over a wide range of state parameters [10].

Figure 1 shows the curve Δλ—ρ for amyl propionate. Such processing was performed over the density range 550-920 kg/m^3, temperature range 425-600°K, and pressure range 0.01-50 MPa for all the ethers studied. The equation of the averaged curve is described by the polynomial

$$\Delta\lambda = \lambda_{P,T} - \lambda_T = \sum_{i=0}^{3} d_i (\rho/1000)^i, \tag{1}$$

where Δλ is the excess thermal conductivity, W/m·deg K; $\lambda_{P,T}$ thermal conductivity of the liquid at temperature T and pressure P; λ_T, thermal conductivity of the gas at temperature T and pressure P = 0.1 MPa; ρ, density, kg/m^3; $d_0 = -0.07672$; $d_1 = 0.41888$; $d_2 = -0.71920$; $d_3 = 0.60472$.

As is evident from the figure, the deviation of some points from the averaged curve comprises 5-6%. Such a scattering of points in the coordinates Δλ—ρ has been observed for other ethers [3]. The presence of such a scattering permits the conclusion that the dependence of Δλ on ρ is ambiguous.

The experimental material on propionate λ was also processed by a method based on the linearity of lines Δλ = const in the P—T diagram [11]. Each line Δλ = const is described by an equation of form P = A + BT. For each set of lines A and B are functions of the excess thermal conductivity only and can be approximated by the polynomials

$$A = \sum_{i=0}^{3} a_i (\Delta\lambda)^i;\ B = \sum_{i=0}^{3} b_i (\Delta\lambda)^i. \tag{2}$$

With consideration of Eq. (2) the calculated equation takes on the form

$$10P = \sum_{i=0}^{3} a_i (\Delta\lambda)^i + \sum_{i=0}^{3} b_i (\Delta\lambda)^i T. \tag{3}$$

The values of the coefficients a_i, b_i in Eq. (3) for isoamyl propionate are presented in Table 5.

Comparison of the propionate λ values calculated by Eq. (3) with experiment shows a divergence of not more than ±1.5%.

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