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THERMOPHYSICAL CHARACTERISTICS OF APROTONIC SOLVENTS AND ELECTROLYTES

BASED ON THEM

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Measured and computed values of the thermal conductivity and heat capacity of a number of organic solvents and electrolytes based on them are presented.

As we have already noted previously [1-2], there are no systematic data in the literature on the physicochemical properties of a comparatively new class of electrolytes (based on organic solvents), which are used in chemical power sources (CPS) with alkali metal anodes [3, 4]. This remark applies to an even greater extent to their thermophysical characteristics as well. At the same time, a knowledge of the latter is necessary for calculations of the thermal operational regimes of these sources.

We studied the temperature dependence of the thermal conductivity of such CPS solvents most widely used in practice: propylene carbonate (PC), γ-butyrolactone (γ-BL), tetrahydrofurane (THF), and their two-component mixtures. Lithium perchlorate (LiClO₄) was used as the ionogenic component of the electrolyte.

The procedure for cleaning and preparing the indicated solvents and electrolytes based on them for the experiment is described in detail in [1, 2].

In order to measure the thermal conductivity, we used the heated-probe method [5], using the apparatus developed at the ITMO AN BSSR [6]. The advantages of this method, which include the short time necessary for the tests (the duration of a single experiment does not exceed 60-90 sec), small overheating of the medium, and good contact between the medium and the sensor, were especially important in application to volatile liquids, such as the substances being studied.

The sensor-probe used in this work consisted of a coil 0.7 mm in diameter and length ~30 mm, made of a bifillar winding on a thin medical needle with diameter 0.5 mm of the heater (consisting of a manganese wire 0.1 mm in diameter with resistance 50-60 Ω) and a resistance thermometer (consisting of copper wire 0.05 mm in diameter with resistance of 3 Ω at 20°C); the probe was covered with a thin lacquer layer for electrical insulation and to increase the mechanical strength.* The dimensions of the probe and of the measuring cell (diameter 30 mm, height 85 mm) permitted us to reduce the intrinsic heat capacity of the former to a minimum and ensure that the boundary conditions of the corresponding heat conduction problem, on whose solution the method is based, are satisfied.

The so-called "relative" variant of the method, in which the thermal conductivity sought is determined by comparing the thermograms recorded on a potentiometer for a standard liquid and for the liquid being studied, is used on our apparatus.

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*The probes had to be changed often due to the strong corrosive action of the solvents studied. Naturally, the new probe required calibration using a standard fluid.

TABLE 1. Values of the Constants Entering into the Equation Approximating the Temperature Dependence of the Thermal Conductivity of Aprotonic Solvents and Electrolytes Based on Them*

Solvent, electrolyte	A, W/m·deg	$B \cdot 10^3$, W/m·deg^2
Propylene carbonate (PC)	$0,227 \pm 0,0060$	$0,703 \pm 0,0925$
γ-butyrolactone (γ-BL)	$0,275 \pm 0,0040$	$0,585 \pm 0,0610$
Tetrahydrofuran (THF)	$0,342 \pm 0,0040$	$0,402 \pm 0,0595$
PC:THF (1:1)	$0,250 \pm 0,0015$	$0,699 \pm 0,0195$
PC:THF (7:3)	$0,240 \pm 0,0060$	$0,679 \pm 0,0895$
γ-BL:THF (1:1)	$0,302 \pm 0,0040$	$0,656 \pm 0,0610$
γ-BL:THF (7:3)	$0,289 \pm 0,0050$	$0,717 \pm 0,0745$
1M LiClO$_4$ in PC	$0,225 \pm 0,0075$	$0,630 \pm 0,1135$
1M LiClO$_4$ in γ-BL	$0,239 \pm 0,0055$	$0,557 \pm 0,0820$
1M LiClO$_4$ in THF	$0,244 \pm 0,0035$	$0,749 \pm 0,0510$
1M LiClO$_4$ in PC:THF (1:1)	$0,238 \pm 0,0085$	$0,573 \pm 0,1295$
1M LiClO$_4$ in PC:THF (7:3)	$0,232 \pm 0,0095$	$0,574 \pm 0,1405$
1M LiClO$_4$ in γ-BL:THF (1:1)	$0,261 \pm 0,0080$	$0,607 \pm 0,1295$
1M LiClO$_4$ in γ-BL:THF (7:3)	$0,254 \pm 0,0065$	$0,566 \pm 0,0925$

*The volume composition is indicated for mixtures of solvents.

A PMS-100 polyorganosiloxane liquid with stable properties was used as a reference. For a specific batch of the substance (according to data obtained at the Tbilisi Affiliate of the D. I. Mendeleev Institute) the temperature dependence of the thermal conductivity is described by the following equation: $\lambda = 0.1685 - 0.175 \cdot 10^{-3} t$, where t is the temperature in °C.

The measuring cell with the fluid being studied and the probe submersed in it was thermostatically controlled for negative temperatures with the help of a TLM thermoelectric refrigerator and an NBE ultrathermostat in the positive temperature range. The measurements were performed repeatedly (up to 10 times) at each temperature level (the points on the graphs are the average values of these measurements).

Prior to performing the experiment, we checked the efficiency of the measuring scheme and the sensors-probes that we made on a number of liquids, in particular, castor oil, for which tabulated data on the thermal conductivity in the temperature range 25-100°C are available. The test gave both qualitative (decreasing temperature dependence), as well as quantitative agreement (the disagreement is within ±5%) with the data in the literature.

The results of the analysis of thermograms are partially presented in Fig. 1 and are generalized in Table 1, which includes the values of constants entering into the equation approximating the temperature dependence of the thermal conductivity $\lambda = A + Bt$. For all the solvents and electrolytes based on them that we studied, these values are determined with a confidence probability of 0.95 from the experimental data, analyzed using the least-squares method.

We first note the increasing temperature dependence of the thermal conductivity of the liquids studied, which is characteristic only for a small class of substances whose molecules contain several hydroxyl groups [7].

Of the solvents studied, the one with the highest thermal conductivity is tetrahydrofuran, followed by γ-butyrolactone and propylene carbonate, which is opposite to the behavior of their viscosity [1]. The thermal conductivity of binary mixtures of these solvents falls between the thermal conductivities of the single component liquids (see Fig. 1) and, in addition, the dependence of the thermal conductivity of the mixture on its composition is curvilinear. For the PC:THF system, variation of the content of the less thermally conducting component (PC) in the mixture over the range from 100 to 50% (volume) has a much smaller effect on its thermal conductivity than in the range 50-0%; for the system γ-BL:THF, this behavior is much less distinct.

The presence of an ionogenic component in the solvent decreases the thermal conductivity of the solution compared to the thermal conductivity of the solvents, which, apparently, can be explained (as can the simultaneous increase in viscosity [1]) by the change in the structure of the liquid, related to the solvation of lithium atoms.

As far as the thermal conductivity of electrolytes based on mixtures of solvents is concerned, the characteristic noted above for binary mixtures of solvents is valid only for the electrolyte based on the system PC:THF; for electrolytes based on the system γ-BL:THF, the thermal conductivity of the mixture is higher than that of its components.
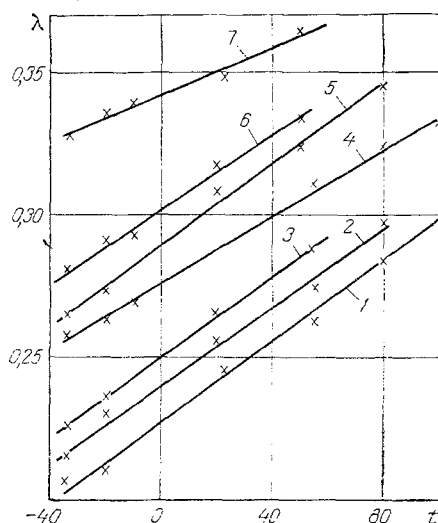
Fig. 1. Temperature dependence of the thermal conductivity (W/m•deg) of aprotonic solvents and their mixtures: 1) PC; 2) PC:THF (7:3); 3) PC:THF (1:1); 4) γ-BL; 5) γ-BL:THF (7:3); 6) γ-BL:THF (1:1); 7) THF.

TABLE 2. Temperature Dependence of the Heat Capacity c_p (J/kg• deg) of Aprotonic Solvents and Electrolytes Based on Them

Solvent, electrolyte	Temperature, °C				
	−30	0	30	60	100
Propylene carbonate (PC)	1990	2260	2550	2870	3310
γ-butyrolactone (γ-BL)	2550	2820	3090	3390	3830
Tetrahydrofuran (THF)	4180	4530	4900	5300	—
PC:THF (1:1)	2530	2830	3150	3500	—
PC:THF (7:3)	2320	2590	2860	3150	—
γ-BL:THF (1:1)	3120	3460	3820	4200	—
γ-BL:THF (7:3)	2850	3170	3490	3840	—
1M LiClO$_4$ in PC	1880	2110	2350	2610	—
1M LiClO$_4$ in γ-BL	2070	2290	2510	2750	—
1M LiClO$_4$ in THF	2130	2650	3300	4130	—
1M LiClO$_4$ in PC:THF (1:1)	2310	2540	2770	3010	—
1M LiClO$_4$ in PC:THF (7:3)	2100	2320	2550	2780	—
1M LiClO$_4$ γ-BL:THF (1:1)	2540	2780	3040	3310	—
1M LiClO$_4$ γ-BL:THF (7:3)	2380	2600	2830	3070	—

Using the experimentally determined values of the thermal conductivity and density [1] of the solvents studied and electrolytes based on them and some empirical equations, it is possible to calculate when necessary two other thermophysical characteristics of the substances: the heat capacity and thermal diffusivity. Table 2 presents the value of the heat capacities of the solvents and electrolytes studied in the temperature range −30-+60°C, calculated using Weber's equation [7] $c_p = 2.79 \cdot 10^7 \lambda / d\sqrt[3]{d/M}$.

We note that for mixtures of solvents and electrolytes, the molar mass was calculated including the molar fractions of the solution components. The average error in the calculation using Weber's equation constitutes ±13%.

From an analysis of the data obtained, it follows that the heat capacities of the solvents and of their mixtures studied are related in the same manner as the thermal conductivities. The heat capacities of all electrolytes are lower than the heat capacities of the corresponding solvents.

NOTATION

λ, thermal conductivity; W/m•deg; t, temperature, °C; c_p, heat capacity, J/kg•deg; d, density, kg/m^3; M, molar mass, kg/kmole.

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THERMAL CONDUCTIVITY OF METHYL AND BUTYL PROPIONATES AT

VARIOUS TEMPERATURES AND PRESSURES

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Experimental data are presented on the thermal conductivities of methyl and butyl propionates in the liquid and gaseous phases, including the saturation line, over the temperature range 300-600°K and pressures of 0.1-50 MPa.

The thermal conductivity of the propionates was studied by the coaxial cylinder method in the stationary regime [1]. Gap thickness in the experimental cell was 0.55 mm for the liquid phase and 0.36 mm for the gaseous phase. Temperature was measured by a 10-Ω platinum resistance thermometer (PTS No. 2000, constructed at VNIIFTRI). Pressure was generated and measured by a class 0.5 piston manometer, type MP-600.

Experimental uncertainties of the thermal conductivity results were $\pm(1.4-2.7)\%$ at a confidence level $\alpha = 0.95$. Purity of the methyl propionate was 99.65%, and that of the butyl propionate 99.76% by weight (measured with "Tsvet-4" chromatograph).

Thermal conductivity was measured along isotherms with temperature steps of 30-35°K and pressure steps of 5-10 MPa. Thermal conductivity of the ethers was studied in the liquid and gaseous phases, including the saturation line. The λ values determined are presented in Tables 1 and 2.

An estimate of the radiant component of propionate λ was performed by studying IR absorption spectra in the wavelength range 2.5-25 μm with an IK-20 infrared spectrometer at 20°C. Analysis of the spectra obtained revealed that the transparency range is narrow and lies within the limits 3.5-5 μm, which corresponds to the maximum of the Planck function, while at temperatures from 116 to 580°K wide intense absorption bands are observed. Calculation of λ_{rad} under these conditions was carried out in the gray approximation [2-6]. The absorption spectra were recorded with a layer thickness d = 0.02 mm, with absorption intensities exceeding 60%, so that the propionates are among the strongly absorbing media. Calculation of the mean absorption coefficient was carried out with Rosseland's formula by the method described in [4]. The resulting value for methyl propionate was $\overline{K}_R = 14.8$ m^{-1}.