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COMPARISON OF THERMAL CONDUCTIVITY OF AQUEOUS AND FORMAMIDE SOLUTIONS ($BeCl_2$) AT HIGH TEMPERATURES

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Abstract- Aqueous solutions of electrolytes are widely used in power plants at thermal and nuclear power plants, installations using solar and geothermal energy, oil and gas industry. In such industries as the production of mineral fertilizers, electrochemical methods for obtaining inorganic metal compounds by electrolysis of aqueous solutions, the production of soda, aqueous solutions of inorganic substances are widely used [1, 2]. This article discusses for the first time experimentally obtained data on the heat conduction of aqueous, as well as formamide solution of $BeCl_2$ at high temperature values. An equation was compiled that makes it possible to forecast the heat conduction of the studied solutions at any electrolyte concentration depending on temperature and pressure.

Keywords: Thermal Conductivity, Formamide, Temperature, Concentration, Pressure, Aqueous Solutions, Concentration.

1. INTRODUCTION

As you know, in many branches of technology there are increased requirements for the accuracy of calculations of technological processes and the reliability of the design of machines and apparatus. The development of industrial and geothermal energy, rocket and cryogenic technology has contributed to a significant expansion of the range of working substances and the range of parameters and has also necessitated the identification of new data on the thermophysical properties of substances necessary to provide a significant economic effect by reducing the cost of fuel, electricity, metal and increasing efficiency technological processes.

Most of the liquids used in modern technology are solutions. The development of processes for the separation, chemical synthesis and purification of substances, the choice of optimal heat and coolants require systematic information on the thermodynamic and transfer properties of solutions. Aqueous electrolyte solutions are widely used in geothermal energy, gallurgy, chemical industry, hydrometallurgy, nuclear power and gas industries.

The study of thermal and transfer properties of aqueous solutions is one of the topical issues of thermophysics and thermochemistry. In our opinion, among the transfer properties of solutions, thermal conductivity is of the greatest interest. Aqueous and non-aqueous electrolyte solutions are increasingly used in various fields of technology, and above all, in industrial power engineering, gallurgy, chemical technology and petrochemistry. Efficient use of aqueous solutions of electrolytes significantly reduces the assessment of their thermophysical properties and, in special, heat conduction in a significant part of the state parameters.

It should be noted that among liquid solutions, aqueous solutions of electrolytes have been theoretically and experimentally most studied, while non-aqueous electrolyte solutions have not received due attention so far, although the study of the behavior of electrolytes in non-aqueous solvents is of great importance for creating the theory of the liquid state in general and the theory of solutions in particular. Therefore, general laws relating to liquids and solutions are difficult to deduce, based on an analogy only with aqueous solutions. In this regard, there is an increasing need to obtain reliable and broader information about the thermophysical properties and, in particular, about the coefficient λ - thermic conductivity of non-aqueous electrolytes.

It is of interest to study the thermal conductivity of formamide and formamide electrolyte solutions at higher parameters in order to more fully determine the nature of the curve $\lambda=f(T)$, the possibility of passing it through a maximum, similar to the curve for the thermal conductivity of water and a number of glycols [3]. The purpose of this work is to obtain experimental results on the thermic conductivity of solutions (aqueous and formamide $BeCl_2$) at high temperature data. Based on these results, equations are derived, with the help of which the thermic conductivity of the studied solutions is calculated at any electrolyte concentration and in a wide range of changes in the state parameters.

2. EXPERIMENTAL METHODOLOGY

Thermal conductivity measurements were performed on a setup that implements the coaxial cylinder method in the relative version, which is described in detail in [4, 5]. We calculate the thermic conductivity coefficient of the solution we study according to Equation (1):

$$\lambda = A\frac{U_2}{\Delta E} \quad (1)$$

where, U is the voltage on the heater; ΔE is the thermoelectromotive force of the differential chromelcopel thermocouple; A is the device constant. According to experimental data A=0.109301 at 20 °C.

When measuring thermal conductivity from 20 °C to 80 °C, atmospheric pressure was taken as the initial pressure, at a temperature of 100-200 °C it was taken from 0.5-50 MPa. The error in determining the thermal conductivity is ± (1.3-1.6) % depending on the temperature.

The solutions were prepared by the gravimetric method from reagents of the "chemically pure" brand. To remove crystallization water, beryllium chlorides were dried to constant weight at 140 °C. The procedure for preparing solutions was the same as in [6]. The installation was calibrated for water. Data on λ of water are taken from [7]. Data on the density of aqueous and formamide solutions of $BeCl_2$ are generally absent in the literature.

As you know, formamide and water are similar to each other; many salts are highly soluble in them; their dielectric permittivity's are large and commensurate; both fluids are associated; the activity coefficients of a number of electrolytes of both solvents change equally with concentration [6]; however, the structure of these liquids is different. Water has a tetrahedral three-dimensional structure, while formamide has a two-dimensional layered structure.

Since the thermophysical properties of formamide are not well understood, we first measure the thermic conductivity of formamide in the temperature diapason (293-473 K). Table 1 shows the obtained experimental data.

Table 1. Experimental meanings of thermic conductivity of liquid formamide depending on temperature, $\lambda\times10^3$, W/mK

T (K)	λ	T (K)	λ	T (K)	λ	T (K)	λ
293	335	333	364	413	385	473	373
303	344	353	373	423	384		
313	352	373	380	433	383		
323	359	393	384	453	379		

As can be seen from Table 1, with increasing temperature, the thermic conductivity of formamide also increases and gets through the highest sloping in the temperature diapason of 393-423 K, as was obtained for water. The results obtained show a similar character of the change in the thermal conductivity of water and formamide depending on temperature, as we assumed in advance. It is shown that at this temperature the thermal conductivity of formamide is 1.8 times lower than the thermal conductivity of water.

The thermic conductivity of aqueous solutions of chlorides of metals of the beryllium subgroup have not been sufficiently studied, and data on λ for aqueous solutions of $BeCl_2$ are generally absent in the literature. In this work, the thermic conductivity of aquatic solutions $BeCl_2$ in the temperature diapason 293-573 K is studied for the first time at seven values of the mass concentration of the solute. The obtained experimental data are shown in Table 2. Figures 1 and 2 show the dependences of the thermic conductivity of aquatic solutions $BeCl_2$ on temperatures and concentration.

Table 2. Experimental values of thermic conductivity of aquatic solutions $BeCl_2$ near the saturation line, $\lambda\times10^3$ W/mK

T (K)	Concentration c, mass %						
	4	8	12	16	20	25	30
293.17	593	588	582	577	571	564	557
303.18	609	603	598	594	586	579	572
313.16	622	616	610	605	599	591	584
323.19	634	628	622	616	610	603	595
333.18	643	637	631	625	619	611	603
353.22	658	652	645	639	633	625	617
373.20	670	663	657	651	644	636	629
393.19	676	669	663	656	651	648	634
413.18	678	671	665	658	652	644	636
423.21	677	670	664	657	651	643	635
433.23	674	667	661	655	648	640	632
453.17	668	661	655	649	642	635	627
473.16	657	651	644	638	632	624	616
493.19	642	636	630	624	618	610	603
498.22	639	631	625	619	613	605	598
523.18	611	605	600	594	588	581	574
533.23	599	594	588	582	577	570	563
543.24	586	581	575	570	564	557	550
548.19	578	574	568	562	557	550	543
553.18	572	566	561	555	550	543	536
573.21	538	533	529	524	519	512	506

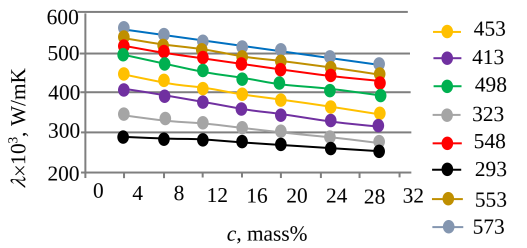

Figure 1. Dependency of the thermic conductivity of aquatic solutions $BeCl_2$ on concentration at various temperatures
1-393 K, 2-353 K, 3-473 K, 4-323 K, 5-523 K, 6-293 K, 7-553 K, 8-573 K

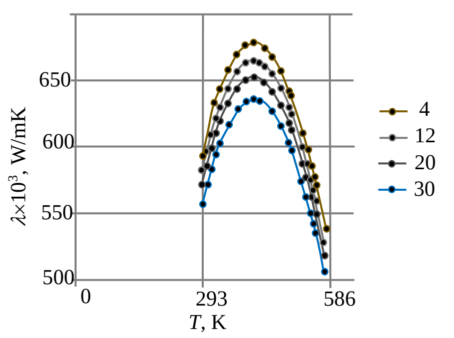

Figure 2. Dependency of thermic conductivity of aquatic solutions $BeCl_2$ on temperatures at various concentrations

Considering that the thermal conductivity of the $H_2O+BeCl_2$ system was studied for the first time, to verify the reliability of the results obtained, we performed calculations using the well-known Equation (2) given in the literature [9]:

$$\lambda_s = \lambda_0 \left(1 - \sum_i \beta_i c_i\right) \quad (2)$$

where, λ_s is the thermic conductivity of the solution; λ_0 is thermic conductivity of water; β_i is coefficients characterizing dissolved substances (salt); c_i is concentration of the solution in units: kg of substance/kg of solution. The thermic conductivity of water in the temperature diapason 0-100 °C is described by Equation (3):

$$\lambda_0 = 0.5545 + 0.00246t - 0.00001184t^2 \quad (3)$$

Table 3 shows the calculated data of the thermic conductivity of aquatic solutions of $BeCl_2$, made according to Equation (3). It can be seen from the table that the calculated and experimental results agree satisfactorily with each other, since the maximum discrepancy is 1.8%.

Table 3. Calculated data of thermic conductivity of aquatic solutions of $BeCl_2$, performed according to Equation (2), and their comparison with experimental data, $\lambda_{calc}\times10^3$, W/mK (* is calculated by Equation (3))

T (K)	λ^*_{calc}	Concentration c, mass %									
		4		8		12		16		20	
		λ_{calc}	Δ, %	λ_{calc}	Δ, %	λ_{calc}	Δ, %	λ_{calc}	Δ, %	λ_{calc}	Δ, %
303	618	612	0.5	606	0.5	601	0.5	595	0.2	589	0.5
323	648	642	1.2	636	1.3	630	1.3	624	1.3	618	1.3
333	659	653	1.5	647	1.5	640	1.4	634	1.4	628	1.4
353	676	670	1.8	663	1.7	657	1.8	651	1.8	644	1.7
373	682	676	0.9	669	0.9	663	0.9	656	0.8	650	0.9

Based on the processing of experimental data, it was found that the thermic conductivity of $BeCl_2$ aquatic solutions in the temperature diapason of 293-573 K is described with an accuracy of ±0.5% by the empirical Equation (4):

$$\lambda_s = \lambda_w \left(1 - 0.01694m - 0.00210m^{\frac{3}{2}} + 0.00190m^2\right) \quad (4)$$

where, λ_s and λ_w are the coefficients of thermic conductivity of the solutions and water; m-molarity. The discrepancy between the calculated values of λ, performed according to Equation (4), and the experimental data is less than ±1%.

In this work, in addition to the thermic conductivity of aquatic solution of $BeCl_2$, the thermic conductivity coefficients of formamide solution of this salt are also determined in the temperature diapason of 293-473 K and concentration (4÷30) mass%. The thermic conductivity of these solution was studied in [9] only at 25°C, depending on the molarity of C_m. For the first time, we studied the thermic conductivity of formamide solution of chlorides of metals of the beryllium subgroup as a function of concentrations, temperatures and pressure.

Our measurements have shown that the effect of electrolytes on the thermal conductivity of formamide is not as strong as that of water. So, for example, for a solution of $BeCl_2$ (c=4 mass%) at 20 °C λ_s is 0.9% less than the thermal conductivity of pure formamide. With an increase in concentration and temperature, the effect of electrolytes on the thermal conductivity of formamide increases; at 200 °C λ_s is 4.8% less than the thermal conductivity of pure formamide. Table 4 below lists the thermal conductivity values of $BeCl_2$ formamide solutions obtained in this work.

Table 4. Experimental data of thermic conductivity of $BeCl_2$ formamide solution, $\lambda\times10^3$, W/mK

T (K)	Concentration c, mass %						
	4	8	12	16	20	25	30
293.16	332	329	326	322	319	315	311
303.19	341	338	334	331	328	324	320
313.17	349	345	342	339	336	331	327
323.18	356	352	349	346	342	338	334
333.22	361	357	354	350	347	343	338
353.13	369	366	363	359	356	351	347
373.14	376	373	369	366	362	358	353
393.18	380	377	373	370	366	362	357
413.24	381	378	374	371	367	363	358
423.13	379	376	372	369	365	361	356
433.19	378	375	371	368	364	360	355
453.25	375	372	368	365	361	357	352
473.21	369	366	363	359	356	351	347

It follows from Tables 2 and 4 that at a given concentrations and temperatures, the ratio of the thermic conductivity of an aquatic solution of $BeCl_2$ to the thermic conductivity of a formamide solutions of the same electrolyte remains constant with an error of (0.56-13)%.

It is interesting to note that the relation of the thermic conductivity of the formamide solutions to the thermic conductivity of pure formamide also remains constant with an accuracy of (0.2-0.3)%. The obtained experimental results on the thermic conductivity of $BeCl_2$ formamide solution are generalized by the parabolic Equation (5):

$$\lambda_s = \lambda_{20} \left(-0.69437 + 2.65408\frac{T}{T_0} - -0.95720\left(\frac{T}{T_0}\right)^2 \right) \quad (5)$$

where, λ_{20} is thermic conductivity of the formamide solutions (20 °C); and T_0 = 293.15 K.

Table 5 shows the calculated data of thermic conductivity obtained by Equation (5) for $BeCl_2$ formamide solutions. The maximum error in determining the thermal conductivity according to Equation (5) is 2% at 200 °C.

Table 5. Calculated values of thermal conductivity of $BeCl_2$ formamide solutions, performed according to Equation (5), $\lambda\times10^3$, W/mK

T, (K)	Concentration c, mass %											
	4		8		12		16		20		25	
	λ_{calc}	Δ, %	λ_{calc}	Δ, %	λ_{calc}	Δ, %	λ_{calc}	Δ, %	λ_{calc}	Δ, %	λ_{calc}	Δ, %
303	341	0.00	338	0.00	335	0.30	331	0.00	327	-0.31	323	-0.31
323	355	-0.28	351	-0.28	348	-0.29	344	-0.31	341	-0.29	336	-0.60
373	376	0.00	373	0.00	369	0.00	365	-0.27	361	-0.28	357	-0.28
423	379	0.00	376	0.00	372	0.00	368	-0.27	364	-0.27	360	-0.28
473	364	-1.37	360	-1.67	357	-1.68	353	1.70	349	-2.01	345	-1.74

Graphical dependences of the thermic conductivity of $BeCl_2$ formamide solution on temperatures and concentrations are not presented in this work, since they are similar to the same dependences of aqueous solutions. The mechanism of heat transfer and other regularities in aqueous and non-aqueous solutions of electrolytes will be discussed in subsequent works.

3. CONCLUSIONS

The thermic conductivity of $BeCl_2$ aquatic solution at high temperatures (T=293.15÷573.15 K) and pressures (p=0.1-50 MPa) was measured for the first time with an error of ±(1.3÷1.6)%. The experiments were performed at concentrations of 4; 8; 12; 16; 20; 25 and 30 mass %. The thermal conductivity of pure formamide was measured at atmospheric pressure in the temperature diapason from 20 to 200 °C. The measurement results confirm the presence of a maximum at a temperature of approximately 120 °C.

An analysis of our experimental and literature data showed that λ formamide, formamide solutions of electrolytes and polyhydric alcohols have maximum values at certain temperatures. It is characteristic that the observed maxima λ of these liquids on the isobars, as well as for water, shift with increasing pressure to the region of higher temperatures.

The anomalous behavior of λ formamide and formamide solutions depending on temperature and pressure is due to the fact that formamide resembles water in its properties: it has a small mole volume (ϑ=40.4) and has a high dielectric constant (ε=108). It is also noteworthy that the nature of the interaction of formamide with water in solution is close to ideal.

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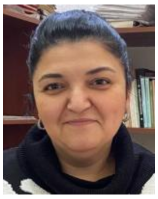

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