Viscosity of Molten Cadmium and Bismuth Chlorides

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Viscosity coefficients of molten $CdCl_2$ and $BiCl_3$ have been measured by the flow-through-capillary method in the temperature ranges from melting points to 965 and 833 K, respectively. The departures from the Arrhenius law at temperatures close to melting points are very small. The Vogel–Tamann–Fulcher three-parameter equation does not constitute a better approximation of the dependences of viscosities on temperature.

Introduction

Molten cadmium and bismuth chlorides pertain to the group of liquids, which are transitory between purely ionic liquids—like molten alkali metal halides—and highly associated molecular liquids represented among inorganic salts by beryllium and mercury chlorides. Molten $CdCl_2$ and $BiCl_3$ show many ionic properties, e.g., rather high electrical conductance; nevertheless they keep some elements of the "covalent structure of their solid state" as "associates" or "autocomplexes". The nature of such species is not completely clear as yet. Coefficients of dissociation of these salts to simple ions increase with temperature, and this effect is manifested by the temperature dependences of some physical properties of these liquids. It has been demonstrated that the ultrasonic velocity in molten $CdCl_2$ decreases with temperature according to a nonlinear law, which is rather untypical for fused inorganic salts (*1*). The temperature dependence of surface tension of the molten $CdCl_2$ demonstrates also some structural rearrangements at temperatures above the melting point (*2*).

It is important to know the temperature dependence of viscosity coefficients of both molten salts, especially in the temperature range close to the melting point when the changes in structure are probably the most distinct. A few authors have measured these parameters in molten $CdCl_2$ and $BiCl_3$. Data concerning molten $CdCl_2$ in the temperature range 863-965 K have been given by Bloom et al. (*3*). The viscosity coefficients of $BiCl_3$ in the temperature range 543-833 K have been determined by Kellner (*4*) as well as by Pustylnyk et al. (*5*). All these measurements have been carried out by the Ostwald–Ubbelohde capillary viscometer method. There is lack of data in the temperature range close to the melting points of both salts.

In the present paper we report the viscosity coefficients of molten $CdCl_2$ and $BiCl_3$ measured in the temperature range starting from their melting points.

Table I. Viscosity Coefficients of Molten $CdCl_2$[a]

expt	temp (±0.1), K	viscosity, cP	expt	temp (±0.1), K	viscosity, cP
I	842	2.62 ± 0.02	II	846	2.522 ± 0.006
	844	2.58 ± 0.03		851	2.49 ± 0.01
	851	2.468 ± 0.008		852	2.47 ± 0.01
	853	2.460 ± 0.005		871	2.39 ± 0.02
	854	2.448 ± 0.009		878	2.24 ± 0.02
	857	2.433 ± 0.005		886	2.256 ± 0.003
	863	2.417 ± 0.001		898	2.164 ± 0.003
	864	2.324 ± 0.009		916	2.08 ± 0.01
	866	2.417 ± 0.009		935	2.01 ± 0.02
	885	2.262 ± 0.007		953	1.91 ± 0.02
	894	2.166 ± 0.002		959	1.87 ± 0.02
	908	2.135 ± 0.005		988	1.779 ± 0.001
	943	1.921 ± 0.002		1002	1.759 ± 0.009
	966	1.843 ± 0.002		1007	1.73 ± 0.01
	968	1.838 ± 0.002		1015	1.699 ± 0.009
	969	1.833 ± 0.008			
	1005	1.799 ± 0.005			

[a] Their values were calculated according to eq 1 by using the mean value of the flow time from four readings.

Table II. Viscosity Coefficients of Molten $BiCl_3$[a]

expt	temp (±0.1), K	viscosity, cP	expt	temp (±0.1), K	viscosity, cP
I	507.0	5.11 ± 0.03	I	648.0	1.17 ± 0.02
	508.5	4.81 ± 0.03		657.0	1.10 ± 0.01
	509.0	4.60 ± 0.05		658.0	1.11 ± 0.03
	510.0	4.51 ± 0.05	II	508.0	5.03 ± 0.02
	511.0	4.278 ± 0.003		521.0	3.593 ± 0.006
	512.0	4.20 ± 0.02		543.0	2.65 ± 0.02
	514.0	4.04 ± 0.02		572.0	2.16 ± 0.04
	536.0	3.1 ± 0.1		630.0	1.40 ± 0.04
	537.0	2.90 ± 0.1		631.0	1.30 ± 0.01
	543.0	2.80 ± 0.06		637.0	1.30 ± 0.02
	553.0	2.488 ± 0.003		652.0	1.14 ± 0.02
	579.0	1.99 ± 0.04		684.0	0.91 ± 0.02
	584.0	1.98 ± 0.08		685.0	0.91 ± 0.01
	585.0	1.90 ± 0.04	III	516.0	4.33 ± 0.02
	593.5	1.776 ± 0.005		546.0	2.773 ± 0.004
	595.0	1.771 ± 0.007		588.5	1.94 ± 0.02
	616.0	1.55 ± 0.04		659.0	1.11 ± 0.02
	635.0	1.47 ± 0.06		676.0	0.99 ± 0.02
	641.0	1.17 ± 0.04		678.0	0.99 ± 0.02
	647.0	1.19 ± 0.02		679.0	0.92 ± 0.05

[a] Their values were calculated according to eq 1 by using the mean value of the flow time from four readings.

Experimental Section

Viscosity coefficients were measured by using a modified quartz capillary viscometer adapted to liquids at high temperatures and in inert atmosphere. Its principle and calibration have been described in a previous paper (*6*). The viscosity coefficients were computed from the flow time according to the known equation

$$\eta/\rho = at + b(1/t) \qquad (1)$$

where η/cP is the coefficient of viscosity, ρ/g cm^{-3} is the density, t is the time of flow through the capillary, and a and b are the viscometer constants. a and b constants determined with H_2SO_4 and KCl aqueous solutions and mercury were $a = (7.78 \pm 0.11) \times 10^{-2}$ cm^2 s^{-2} and $b = -5.02 \pm 0.52$ cm^2.

The density data reported by Mościński and Suski for molten $CdCl_2$ (*7*) and by Keneshe'a and Cubicciotti for molten $BiCl_3$ (*8*) have been used.

Cadmium chloride (analytical grade from POCh, Gliwice, Poland) and bismuth chloride (reagent grade from USSR) have been dehydrated as discussed previously (*9*) and used for measurements. The filling of the viscometer with salts, evacuation, and

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Table III. Values of Constants in Arrhenius and VTF Equations Calculated for Data in Tables I and II

	Arrhenius equaiton $\eta = Ae^{B/T}$			VTF equation $\eta T^{-1/2} = Ae^{B/(T-T_0)}$			
	ln *A*	*B*	correlation coeff	ln *A*	*B*	T_0, K	correlation coeff
$CdCl_2$	−1.47 ± 0.05	2019 ± 42	0.9936	−3.97 ± 0.02	559 ± 103	475 ± 2.5	0.9971
$BiCl_3$	−4.68 ± 0.09	3137 ± 50	0.9953	−6.14 ± 0.05	1312 ± 214	215 ± 2.5	0.9971

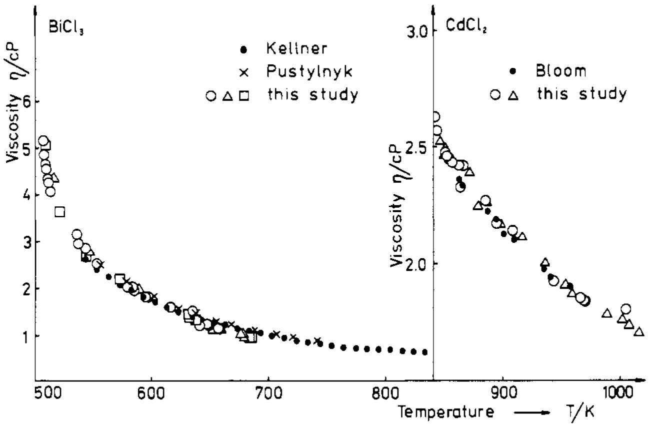

Figure 1. The temperature dependence of viscosity of molten $BiCl_3$ and $CdCl_2$.

refilling with helium were carried out as previously described (*6*, *9*).

Results and Discussion

The results of our measurements are reported in Tables I and II. They are compared with data of previous authors on Figure 1. The agreement of all sets of values is satisfactory.

Due to the supposed structural rearrangements occurring in both salts with increasing temperature, one should expect the dependences rather nonconforming to the Arrhenius law. Our experimental results show a small departure from this law only in the lowest temperature region of existence of the liquid phases. This departure is more distinct in the $BiCl_3$ than in the $CdCl_2$ case.

The three-parameter equation of Vogel-Tamann-Fulcher (VTF) type (*10*-*12*)

$$\eta / T^{1/2} = Ae^{B/(T-T_0)} \qquad (2)$$

where η is the viscosity coefficient, T/K is the temperature, T_0/K is the temperature of the ideal glass transition, and A and B are constants, does not approximate the experimental data better than the Arrhenius law.

Table III reports the values of constants and correlation coefficients calculated by fitting our results for both Arrhenius and VTF equations. The reported B and T_0 values correspond to the highest correlation coefficient for the logarithmic form of eq 2 when all our experimental data in the full temperature range are used.

It should be noted that the dependences on temperature of the viscosities of both salts demonstrate the structural anomalies different than the ultrasonic velocities. In the case of $CdCl_2$ the latter property depends on temperature according to the nonlinear law (*1*), whereas the same dependence for $BiCl_3$ is linear (*13*). So ultrasonic properties indicate the more distinct structural rearrangement in molten $CdCl_2$ than in $BiCl_3$ whereas viscosity data suggest the opposite conclusion.

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Development of an Apparatus To Measure Vapor Pressures at High Temperatures and Its Application to Three Higher-Boiling Compounds

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An apparatus to measure vapor pressures of aromatic hydrocarbons up to moderately high temperatures is described. With this apparatus, the vapor pressures of tetralin, *m*-cresol, and biphenyl were measured up to 600.7 K. The measurements are found to be in agreement with selected literature values, measurements of which have been conducted previously.

Introduction

An accurate knowledge of vapor pressures is needed for several theoretical and practical reasons. Such data are needed to establish pure-component limits in binary systems and liquid-activity coefficients in multicomponent systems, for the calculation of enthalpy of vaporization, etc. Also, vapor pressure data are needed to obtain enhancement factors which help in

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