molar heat of solution for CA in water at 298.15 K obtained from solubility data is 145.4 ± 3.0 kJ/mol.

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Viscosity of Molten Alkaline-Earth Chlorides

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Precision determinations of the viscosities of four molten alkaline-earth chlorides are reported. The following equations express the results in mPa s with 0.06–0.19% standard deviation: $MgCl_2$, $\eta = 0.17985 \exp(2470.1/T)$; $CaCl_2$, $\eta = 0.28498 \exp[1373.5/T + (1.258 \times 10^6)/T^2]$; $SrCl_2$, $\eta = 0.36396 \exp[917.0/T + (2.024 \times 10^6)/T^2]$; $BaCl_2$, $\eta = 0.23452 \exp[1946.8/T + (1.828 \times 10^6)/T^2]$. The accuracy estimate is 0.3% on the 68% confidence level. Present data for $CaCl_2$, $SrCl_2$, and $BaCl_2$ deviate 7–12% from previous recommendations. Some comments on the responses of oscillational viscometers are given together with a brief discussion of the results.

Introduction

When one reviews theories for the molten state proposed from observations of transport properties, it becomes apparent that these properties are disappointingly insensitive to differences in liquid structure and that quite accurate data are needed if they are to reveal even major structural changes. It follows that abrupt and dramatic fluctuations in, for instance, the viscosity as a function of temperature and/or composition should not be expected, the continuing appearance of reports to the contrary notwithstanding.

Even today, only a few high-temperature fluids have been investigated with an accuracy that permits the attention to be focused squarely on liquid characteristics rather than experimental artifacts. The present work is part of a program at this laboratory to establish accurate values for the viscosity of molten alkali-metal halides and alkaline-earth halides.

Experimental Section

The viscometer operates by measuring the damping and the time-of-swing of an oscillating noble-metal cylinder. Absolute viscosities are obtained from both types of data without the need of calibration against reference liquids, as described elsewhere (*1*). The method is considered superior to other techniques that we know have been applied to high-temperature liquids, oscillating sphere viscometers included. A similar hollow-cylinder (cup) version, which is useful for very volatile or corrosive liquids although less accurate because of the meniscus effect, is discussed in ref *2*. We have recently commented upon both cylinder and cup oscillational viscometers and high-temperature viscometry in general (*3*). That comment also refers to our available computer programs developed and used in this laboratory for obtaining accurate logarithmic decrements and time-of-swings from a very simple experimental setup, involving two permanently fixed photodetectors and a nonadjustable laser.

Chemicals used were $MgCl_2 \cdot 6H_2O$ (Baker, analytical reagent), $CaCl_2 \cdot 2H_2O$ (Merck, p.a.), $SrCl_2 \cdot 6H_2O$ (BHD analytical) and $BaCl_2 \cdot 2H_2O$ (Merck, p.a.). All salts were purified by passing HCl gas through the samples at temperatures rising from 25 to 400 °C. They were later heated at 400 °C for 0.5 h under 0.01–0.05 Pa in the viscometer furnace immediately before runs. In addition, $MgCl_2$ was melted after the initial treatment with HCl, again treated with HCl, and then filtered and distilled twice on a vacuum line.

After purification, the samples were prepared and handled as previously described for the alkali-metal chlorides (*4*). A low bulk density of the $BaCl_2$ sample made it necessary to premelt part of the charge. Drybox techniques were used in all stages, and the viscometer was purged with highly purified nitrogen.

Gas bubbles, a potential source of serious errors (*4*), did not form on the oscillating cylinder surfaces according to the following criteria: moving the sample-containing crucible repeatedly up and down did not change the viscosity as calculated from either the oscillation period or the damping constant; "period" viscosities agreed with "damping" viscosities within the normal experimental uncertainty; results did not show any correlation with the temperature history of the sample. A quasi-random selection of experimental temperatures could thus be made in contrast to the alkali-metal chloride work. The same measuring procedure was otherwise followed with a few exceptions: the number of oscillations had to be reduced to the 15–30 range because of the high damping, experiments were not repeated with other, independently prepared samples, and the upper temperature limit was that for which recommended density data exist.

Evaporation losses were less than 1% for $CaCl_2$, $SrCl_2$, and $BaCl_2$. It was not determined for $MgCl_2$ as this salt was recovered for later use. Approximate melting points were measured upon completion of the experiments by observing freezing plateaus in situ (no stirring was possible). A pH determination was performed on one salt—$SrCl_2$—after the experiment.

As usual, the investigation was preceded by a series of control experiments in water. Temperatures were measured with a mercury-in-glass thermometer calibrated at the National Physical Laboratory, England. Readability and calibration was 0.002 °C.

Results

The damping of a body oscillating in a fluid depends upon the density of the fluid as well as its viscosity, and the density must

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Table I. Viscosities (η) of $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$

temp, °C	η, mPa s	$10^{-4}\cdot$(SD),[a] mPa s	temp, °C	η, mPa s	$10^{-4}\cdot$(SD), mPa s
		$BaCl_2$			
998.5	3.3711	13	1020.7	3.1427	10
	3.3705	15		3.1415	8
	3.3711	13		3.1428	13
	3.3701	13		3.1414	10
	3.3705	13	1000.6	3.3279	20
1077.2	2.7046	14		3.3295	14
	2.7034	12		3.3287	17
	2.7041	9		3.3302	13
	2.7050	15	979.8	3.5503	14
1040.0	2.9806	16		3.5504	10
	2.9779	16		3.5506	19
	2.9812	14		3.5514	14
	2.9794	16	966.0	3.7092	12
1098.6	2.5617	9		3.7097	14
	2.5613	9		3.7101	11
	2.5617	9		3.7095	13
	2.5615	13			
1061.1	2.8138	9			
	2.8144	11			
	2.8148	8			
	2.8153	11			
		$SrCl_2$			
940.6	3.0644	10	1000.2	2.6071	13
	3.0631	13		2.6072	13
	3.0630	15		2.6061	16
	3.0626	14		2.6058	13
	3.0640	8	939.6	3.0689	17
1045.0	2.3384	12		3.0671	18
	2.3391	11		3.0674	15
	2.3387	11		3.0667	11
	2.3394	8	908.9	3.3626	17
970.5	2.8162	10		3.3658	13
	2.8158	9		3.3637	18
	2.8160	10		3.3618	20
	2.8162	14	878.9	3.7082	14
1029.5	2.4250	10		3.7072	15
	2.4257	11		3.7077	15
	2.4252	12		3.7092	15
	2.4246	14			

temp, °C	η, mPa s	$10^{-4}\cdot$(SD),[a] mPa s	temp, °C	η, mPa s	$10^{-4}\cdot$(SD), mPa s
		$CaCl_2$			
831.2	2.7698	8	802.1	3.0350	11
	2.7694	15		3.0361	19
	2.7700	14		3.0344	11
	2.7701	11		3.0352	14
888.8	2.3593	10	786.4	3.1968	15
	2.3591	8		3.1957	11
	2.3599	8		3.1967	15
	2.3591	8		3.1965	13
965.5	1.9593	7	799.9	3.0572	11
	1.9600	6		3.0584	19
	1.9595	6		3.0567	17
	1.9599	11		3.0561	19
860.3	2.5493	6	771.2	3.3640	32
	2.5494	8		3.3644	29
	2.5479	10		3.3644	22
	2.5503	9		3.3610	16
949.5	2.0335	8	741.1	3.7506	21
	2.0334	7		3.7472	18
	2.0338	9		3.7467	42
	2.0340	10		3.7432	15
919.7	2.1832	11	713.9	4.1717	13
	2.1826	10		4.1710	15
	2.1832	8		4.1687	17
830.6	2.7801	7		4.1666	19
	2.7793	8			
	2.7800	8			
	2.7797	11			
		$MgCl_2$			
899.6	1.4768	8	810.8	1.7573	7
	1.4776	7		1.7595	9
	1.4773	10		1.7578	11
	1.4769	11		1.7580	9
839.9	1.6548	10	780.1	1.8792	9
	1.6553	8		1.8778	8
	1.6557	8		1.8786	11
	1.6559	6		1.8783	8
750.6	2.0094	15	720.1	2.1605	10
	2.0106	16		2.1586	13
	2.0093	15		2.1613	10
	2.0087	17		2.1614	12
869.3	1.5608	5	779.4	1.8788	8
	1.5615	9		1.8791	8
	1.5608	9		1.8790	8
	1.5606	11		1.8795	10

[a] Standard deviation calculated from the SD in the logarithmic decrement.

be known to about the same accuracy as that required in the viscosity. The density equations of Bockris et al. and van Artsdalen et al., recommended by Janz et al. (*5*), were used in computing viscosities (densities in units of g/cm^3).

$$MgCl_2 \qquad \rho = 1.976 - (0.302 \times 10^{-3})T \qquad (1)$$

$$CaCl_2 \qquad \rho = 2.5261 - (0.4225 \times 10^{-3})T \qquad (2)$$

$$SrCl_2 \qquad \rho = 3.3896 - (0.5781 \times 10^{-3})T \qquad (3)$$

$$BaCl_2 \qquad \rho = 4.0152 - (0.6813 \times 10^{-3})T \qquad (4)$$

Experimental results are given in chronological order in Table I. The following modified Arrhenius model (*2*, *6*) was fitted to the data:

$$\eta = A \exp\{B(1/T - 1/T_m) + C[(1000/T - k)^m - (1000/T_m - k)^m]\} \qquad (5)$$

The exponent m is always assigned the lowest integer value consistent with the experimental accuracy; that is, increasing m further should not improve significantly the standard deviation of the fit. Noninteger values for m are permitted, but seldom, if ever required. In this work, $m = 0$ ($MgCl_2$) or $m = 2$ ($CaCl_2$, $SrCl_2$, $BaCl_2$). The parameter k, equal to $1000/T_u$ where T_u is an approximate extremal temperature, and the experimental mean temperature T_m are introduced to suppress the correlation between A, B, and C. Apart from reducing convergence problems in the parameter estimation, this reparametrization has the advantage of providing a nearly orthogonal higher-order term which therefore is a measure of the curvature in the log η vs. $1/T$ relationship (*6*). Table II contains the fitted parameters A, B, C with standard deviations. Curves calculated from eq 5 are shown in Figure 1 together with experimental data points.

Inserting the fitted parameters into eq 5 and rearranging yield a set of viscosity equations that are easier to use:

$$MgCl_2 \qquad \eta = 0.17985 \exp(2470.1/T) \qquad (6)$$

$$CaCl_2 \qquad \eta = 0.28498 \exp[1373.5/T + (1.258 \times 10^6)/T^2] \qquad (7)$$

$$SrCl_2 \qquad \eta = 0.36396 \exp[917.0/T + (2.024 \times 10^6)/T^2] \qquad (8)$$

$$BaCl_2 \qquad \eta = 0.23452 \exp[1946.8/T + (1.828 \times 10^6)/T^2] \qquad (9)$$

Table II. Parameters in the Exponential Temperature Function Eq 5 for the Viscosity of Molten Akaline-Earth Chlorides

salt	temp span, K	data points	A, mPa s	$10^{-4}\cdot$ (SD),[a] in A, mPa s	B, K	SD[a] in B, K	C, K^2	SD[a] in C, K^2	k, K^{-1}	m	SD[a] in η, %	T_m, K	η at 1240 K, mPa s
$MgCl_2$	993-1173	32	1.7733	3.0	2470.1	3.4				0	0.09	1079.37	1.318[b]
$CaCl_2$	987-1239	51	2.7518	3.8	3386.3	6.5	1.258	0.03	0.80	2	0.06	1106.90	1.955
$SrCl_2$	1152-1318	33	2.8704	4.4	3953.0	12	2.024	0.09	0.75	2	0.06	1236.59	2.844
$BaCl_2$	1239-1372	37	3.0982	15	4506.0	86	1.828	0.06	0.70	2	0.19	1299.35	3.701

[a] SD = standard deviation. [b] Extrapolated 67 K.

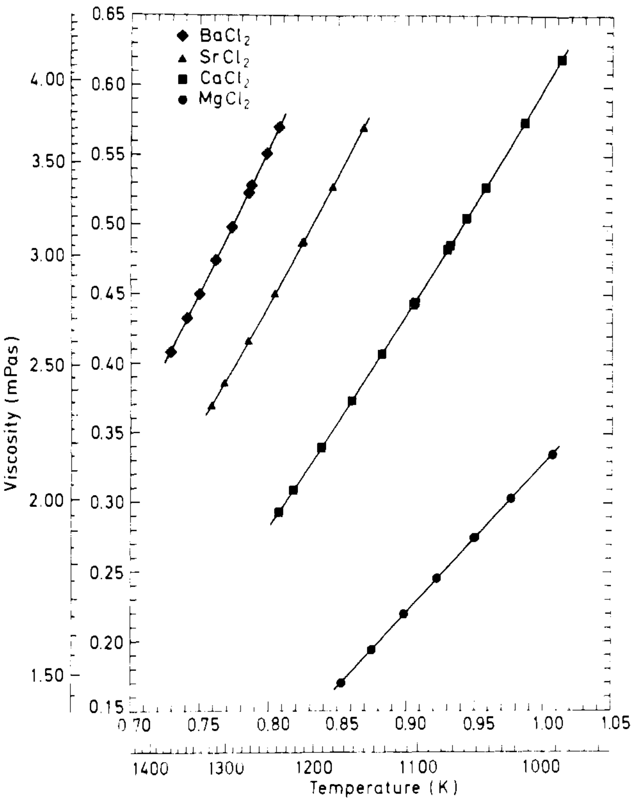

Figure 1. Arrhenius plots (log η vs. $1000/T$) of the viscosities of molten alkaline-earth chlorides. Symbols represent mean experimental values. Curves calculated from eq 5.

The viscosities are in mPa s (=centipoise).

Equation 10 has been found valid for several molten salt

$$\Delta\eta(\%) = -0.8\Delta\rho(\%) \qquad (10)$$

systems (*1*, *4*, *6*, *7*). On the left-hand side is the percent change in the viscosity caused by a $\Delta\rho$ percent revision of the adopted density. Equation 10 has not been fully verified for the present alkaline-earth viscosities but can probably be applied for density revisions not exceeding ±2%.

Observed melting points (freezing plateaus in the absence of stirring) agreed with values recommended by Janz et al. (*5*) within 1 ($MgCl_2$, $SrCl_2$) and 2 ($BaCl_2$) °C. There is a 10 °C conflict between Janz et al. (*5*) and Barin and Knacke (*8*) regarding $CaCl_2$; our result is within 1 °C of the melting point 772 °C quoted by the latter authors.

Pronounced supercooling occurred in the $CaCl_2$ melt, which remained liquid down to 693 °C before the onset of solidification. The lowest data point in Table I is 58 °C below the melting point. The internal consistency of the experimental data did not suffer in going into the supercooled region, which indicates both that the liquid behaved in a normal Newtonian fashion and that the density data were sufficiently accurate despite the extrapolations required. There is no discontinuity in the temperature response at the melting point.

Some color changes from the original pure white could be seen in $BaCl_2$ and $SrCl_2$ upon removal from the viscometer after runs. The $BaCl_2$ salt had a brownish tinge. $SrCl_2$ formed large, clear crystals with a weak yellow-brown color. A solution of 2 wt % of the latter salt in water had a pH of 8.8.

Eight successive determinations of the viscosity of water at 24.926 °C were performed within 1 h. The temperature was kept constant to 0.002 °C. The obtained mean value 0.8913 mPa s, standard error 0.000 06 mPa s, is 0.04% below the recommended (*9*) value 0.8917 mPa s.

Discussion

Our third-generation viscometer has been discussed extensively in previous publications (*1*, *2*, *10*), and most recently in connection with our report on alkali-metal chloride viscosities (*3*, *4*).

We have noted lately that the mechanical properties of our 92% Pt-8% W torsion wire tend to change when it is taken from spools of different batch numbers. The internal friction of the wire— measured at less than 0.01-Pa gas pressure— may vary considerably, and likewise the torsion coefficient. Also the amplitude dependency of those two properties is affected. Present values for the increase in the period and the damping constant with increasing amplitudes are thus about one-fourth of the coefficients given in ref *1* for the original wire. The nonharmonic behavior is now nearly undetectable.

Changes in the axial load on the wire cause elongations or contractions which require the measured angular moment of inertia of the oscillating system to be corrected to zero load change. All periods measured in liquids are corrected for the same reason (*1*, *10*). Again, such corrections appear to be batch dependent.

Moreover, it is our experience that the torsion wires are sensitive to sudden shifts in the tension on the wires, beside undergoing secular changes under conditions of constant load. This is more serious than batch-related variations since frequent redeterminations of the various corrections are necessary in careful work, e.g., at better than 0.5-1% accuracy. Ultimately, the inherent instability of the wire will limit the accuracy obtainable with oscillational viscometers. However, this limit is probably somewhere below 0.1% when all possible precautions are taken and the viscometer designed to minimize the consequences of unavoidable microfluctuations in the wire structure.

We recommend against methods which are based on the assumption that the zero base line of the oscillations is the same as the rest position observed before (or after) the run. Our procedure is to calculate, without approximations, the oscillation zero using the method of timed intervals (*1*, *3*, *11*), that is, from information recorded while the system is oscillating. This base line certainly varies from experiment to experiment to a small, but not negligible, extent, and the shifts seem unrelated to the visually observed movements of the rest position of the oscillating assembly.

The present study is a direct continuation of our work on alkali-metal chlorides, and the accuracy estimate of 0.3% given in ref *4* applies also here. This estimate does not include the

Table III. Deviation (in %) of Recommended (*5*) Alkaline-Earth Viscosities from Present Values[a]

temp,[b] K	$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$
1000	+0.6			
1060	+0.6	+6.6		
1140	0.0	+7.1		
1160		+7.1	+9.4	
1220		+8.5	+7.4	
1240			+8.3	
1250				+12.1
1340				+8.1

[a] Table II; eq 5. [b] Experimental limits (*5*).

effect of errors in the adopted densities, but eq 10 can be used to correct for minor revisions of the density data. Measured viscosities are reproducible to considerably better than 0.3% as found by comparing independent series of runs in identical systems (e.g., ref *1* and *4*), and from the scatter in the viscosity vs. temperature model fits. Table II shows that the SD in the fits for the alkaline-earth chlorides is in the 0.05–0.1% range, except for $BaCl_2$. Better fits have been obtained, e.g., 0.03% for molten NaF (*7*), while the 0.19% SD for barium chloride is about the largest observed in systems where the presence of gas bubbles or particulate matter is not otherwise suspected.

The control measurements in water were made near 25 °C with an estimated accuracy of 0.11% (*1*). This root mean square value resulted from an error analysis at a very early stage in the construction and testing of our latest viscometer. It has been supported by a number of experiments in water, the present included, since the instrument came into regular use around 4 years ago. We have so far never deviated more than 0.09% from the recommendation (*9*), which in the temperature region of interest relies essentially on Swindells' protracted series of experiments with a capillary viscometer at the U.S. NBS. Our somewhat broader error limits in high-temperature media are mainly intended to absorb temperature measurement errors.

The measured melting points and the single pH determination indicate that the salts were at least not grossly contaminated, although the 1–2 °C agreement between measured and reported melting points is admittedly a better check on the accuracy of the temperature readings than on specimen purity. We assume as usual that the in-house calibrated type-S thermocouples are accurate to within 1 °C, which is consistent with the noted agreement considering that the determinations were made in situ and not in a thermal analysis apparatus. The color change in $BaCl_2$ and $SrCl_2$ from pure white is probably due to introduction of trace oxygen in the crystal lattice. Such changes are commonly observed in pure salts, albeit rarely mentioned. They are not related to chemical impurities that would affect the viscosity.

Table III contains a comparison of our present results with the recommendations of the Molten Salt Data Center (MSDC) (*5*). The recommended viscosities are for $CaCl_2$, $SrCl_2$, and $BaCl_2$ based on the investigations of Costin and Zuca (*12*), and for $MgCl_2$ on an averaged equation generated from the works of Bondarenko and Strelets (*13*) and Dumas et al. (*14*), the last from this laboratory. All workers except the present have used the oscillating sphere technique.

The agreement for $MgCl_2$ is comfortably within the uncertainty associated with the dimensional inaccuracies of noble-metal spheres. Viscometers employing such spheres are at best capable of ±2–3% accuracy (*1*, *15*). Calibration against reference liquids may yield an improved effective sphere radius, but the viscometer then no longer operates as an absolute instrument. It is our opinion that the numerous conflicts between reported viscosities of high-temperature corrosive fluids sometimes can be ascribed to radius calibration errors. Where close agreement among erroneous results occurs—cryolite is a prime example (*7*, *16*)—it is the most reasonable explanation, and we suspect the erroneous set of too high NaCl viscosities formerly used for reference purposes to be mainly responsible. Noble-metal cylinders (or cylindrical cups) can be machined so accurately that the resulting uncertainty in the viscosity is better than 0.1% (*1*, *10*), and no calibration is necessary.

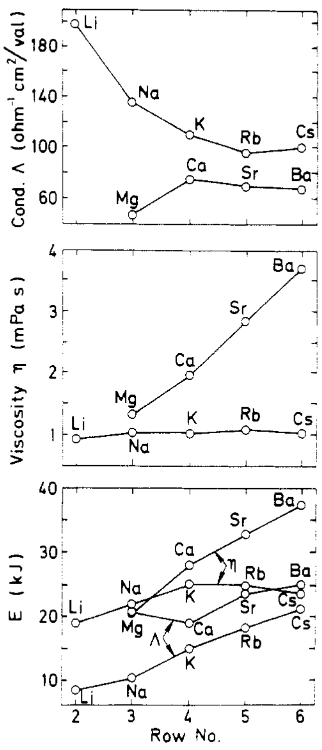

Figure 2. Equivalent conductance (upper diagram) and viscosity (middle diagram) for group 1 and group 2 chlorides at 1073 and 1240 K, respectively, plotted against periodic system row number. Lower diagram depicts activation energies for viscous flow and electrical transport. Conductance data for NaCl, KCl, $MgCl_2$, $CaCl_2$ from Grjotheim et al. (*18*), otherwise MSDC (*5*). Viscosity data from ref *4* and this work with activation energies taken from our exponential factor *B*.

MSDC assigns an uncertainty of around 2.0% to the recommended viscosity for $MgCl_2$. No accuracy estimate is given for the other recommendations, which are 7–12% higher than present results. This tendency toward too high viscosities is fairly common in earlier investigations. Unsuspected gas bubbles adhering to the oscillating body can cause errors of this magnitude (*4*), but, since no evidence of bubble formation in alkaline-earth chlorides was found in this work, the reason for the discrepancy probably lies elsewhere.

Earlier work at this laboratory (*14*, *17*) with our first-generation, oscillating sphere viscometer compares with present values as follows (1073 K): -0.4% ($MgCl_2$), -0.7% ($CaCl_2$). The agreement is within +0.2%, -1.2% at all temperatures for both salts.

Molecular dynamics calculations, which yielded promising results for two alkali-metal chlorides (*4*), appear not to have been applied to any of the salts studied here. We refrain from interpreting our results in terms of a model for the molecular structure of alkaline-earth chlorides. The guiding principles that have been set forth need a larger body of accurate experimental data to lose their ad hoc character and attain some predictive power. Viscosity data for four different liquids are not sufficient. However, a few comments are in order.

Figure 2 shows how the viscosity and the closely related equivalent conductance of the group 1 and 2 chlorides vary with their position (row number) in the periodic system: (a) The alkali-metal chlorides all have the same viscosity within a few percent, unaffected by the increasing size and mass of the cation. The activation energy for viscous flow is also nearly constant. (b) Viscosities and activation energies increase from $MgCl_2$ to $BaCl_2$. (c) Equivalent conductances decrease and activation energies increase from LiCl to CsCl. (d) There is a maximum in the conductance curve for the alkaline-earth chlorides at $CaCl_2$, caused by a relatively low value for $MgCl_2$. The activation energy is nearly constant (cf. below for data reliability).

These features conflict with chemical intuition: where one group behaves "ideally" in the sense that the property under consideration changes in a more or less regular fashion as one descends the ladder of the periodic system, the other property does not, and the property that has this ideal aspect in one group is the one that shows anomalies in the other group. Furthermore, anomalies for LiCl and $MgCl_2$ could reasonably be expected—almost demanded. They are remarkably absent except for the low conductance of $MgCl_2$, which is not dramatically low (30% under that of $BaCl_2$).

The conductance of $MgCl_2$ has been taken as evidence of covalent bonding. This leaves the problem of explaining a viscosity that by the same line of reasoning is quite normal. Neither do the activation energy curves in Figure 2 reflect this proposed structural different from the other group 2 chlorides. The low conductance of $MgCl_2$ is the *only* sign of covalency, and no more spectacular than some other features in Figure 2. We are aware that there is considerable evidence for the complex-forming ability of the Mg^{2+} cation in mixtures with other chlorides. The point that we wish to reiterate here is that macroscopic transport properties are not easily predicted even for relatively simple liquids.

Different authors disagree on the activation energies of electrical transport to an extent that makes details in the corresponding curves in Figure 2 uninteresting. If only MSDC-recommended values are considered, for example, then the weak minimum for $CaCl_2$ disappears completely. It might also be noted that the activation energy for viscous flow is slightly temperature dependent for $CaCl_2$, $SrCl_2$, and $BaCl_2$ according to Table II.

Plotting against the size or mass of the cations is no more illuminating than the row number selected in Figure 2. Interestingly, the lanthanide contraction in the radii of the alkaline earths is not usually met with a corresponding reduction in the transport properties, which causes several artificial-looking maxima and minima to emerge if the radius is chosen as the plotting parameter.

All pure salts hitherto examined by our latest viscometer (alkali-metal chlorides (*4*) and NaF (*7*)) have had one characteristic in common—they follow the Arrhenius (or Kelvin) temperature rule within 0.1% over the entire experimental range of temperatures. So do salt mixtures in which there is little evidence of shifting chemical equilibria (*2*, *7*, *6*, *10*). In the opposite case, the curves have always been nonlinear, and without exception concave upwards. Aluminum chloride is in a special class, since the Arrhenius plot for the pure compound is concave downwards (*2*). However, this is exactly what must be expected for a liquid that approaches its critical point. Although the validity of the Arrhenius rule has been questioned for constant-pressure transport processes, and a number of other temperature functions have been proposed, we arrived at the tentative conclusion that deviations are essentially associated with a liquid structure in which several species coexist in concentrations that depend on the temperature. This assumption worked well in several models for complex-forming liquids (*2*, *7*, *6*, *10*). The slight, but significant, deviations exhibited by $CaCl_2$, $SrCl_2$, and probably $BaCl_2$ are therefore disturbing to us. Almost as puzzling is the fact that the single salt which does not deviate is precisely that which was expected to do so, namely, $MgCl_2$. More data of accuracy and precision similar to the present are needed to determine what the typical temperature response—if any—of the group 1 and 2 halides is.

Acknowledgment

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Low-Temperature Heat Capacities of Sodium Hexatitanate

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Low-temperature heat capacities of sodium hexatitanate, $Na_2Ti_6O_{13}$(c), were measured at the U.S. Bureau of Mines over the nominal range 5.5–308 K by using precision adiabatic calorimetry. The standard entropy, $S°_{298.15}$, of 95.27 ± 0.3 cal K^{-1} mol^{-1} was derived assuming $S° = 0$ at 0 K.

Introduction

This investigation is part of a Bureau of Mines program to provide basic thermodynamic data useful to the mineral and chemical industries. Previous Bureau studies (*1*, *2*) have determined formation enthalpies and entropies of several closely related sodium titanates. The present study provides low-tem-