Corresponding-States Data Correlations and Molten Salts Viscosities[1]

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Transport properties of molten salts are encountered in a broad range of R&D tasks, particularly in areas of high-temperature thermal energy storage and in advanced battery concepts. This communication examines a semiempirical corresponding-states correlation as a predictive method using molten salts viscosities. Predictive calculations with molten NaCl and KNO_3 as model systems, and with calibration quality data sets as the reference base, are used to evaluate this method. While the proper slope for the temperature dependence is "forecast," the quality of the predicted data depend directly on the accuracy level of the one experimental value that is the seed for the calculations. Some results are described to show how such calculatins have proved useful in guiding value judgments in studies of the viscosity data in the open scientific literature.

KEY WORDS: corresponding-states relation; fused salts; molten salts; potassium nitrate; sodium carbonate; sodium chloride; viscosity.

1. INTRODUCTION

Molten salts are encountered as working fluids in various electro-mechanical and metallurgical processes and, more recently, as candidate systems in a diverse range of energy-related R&D projects, such as low-quality heat utilization studies, e.g., solar heat, industrial waste heat, or again, in advanced battery and fuel cells concepts. Because such salt

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systems have moderately high melting temperatures, measurements of properties such as viscosity are not simple matters. Therefore it has become important to accumulate reliable experimental data and to establish predictive methods to enable "forecasts" for situations where measured values are minimal, and even nonexistent.

In this paper we report the results for some studies in progress in which empirical and semiempirical corresponding-states correlations are being evaluated. Some of the theoretical studies that underlie corresponding-states transport properties calculations and some of the work with molten salts in this area are first briefly reviewed as background to the present study. The quality of the experimental data base is another consideration and this factor is also considered. The utility of a semiempirical corresponding-states correlation equation for viscosities is then examined as a predictive method, with NaCl and KNO_3 as model systems, and further tested with the data for a series of molten salts.

2. BACKGROUND STUDIES

In the concept of the principle of corresponding states, values of bulk properties are transformed to reduced values through operations with the values of these when the materials are at a predefined characteristic state. The equation of state expressed in these reduced properties, i.e., the reduced equation of state, has been markedly successful as a correlation equation for a broad range of gaseous and liquid fluids. This has led to a series of studies of predictive methods based upon theoretical, semiempirical, and empirical principles in this area of physical and materials science. The detailed consideration of these falls outside the intent of this paper, and it is sufficient to note briefly some of the contributions that have bearing on the topic of concern in the present communication.

The principle of corresponding states was placed on a firm theoretical basis through studies, such as Pitzer [1], that focused on linking bulk thermodynamic properties and microscopic molecular properties through the methods of statistical mechanics. The molecular basis for reducing transport properties followed with solutions of the mechanical equations of motion in reduced variables [2, 3] and this area has continued through to the present date as a fertile field for fundamental and applied studies. Basic understandings of molecular processes in fluids have contributed to advances in process design studies, and to generalized correlations for both thermodynamic and transport properties for a broad range of fluids; see Renon et al. [4], Flynn and Thodos [5], and Chung et al. [6].

Concerning molten salts, studies of the corresponding-states principle have somewhat paralleled the preceding advances. Theoretical studies, such

as that by Reiss et al. [7], investigated the applicability of this approach to purely ionic salts in the molten state from the viewpoints of statistical mechanics. Extension of the corresponding-states principle to transport properties of molten salts have followed through theoretical and semi-empirical studies. Abe and Nagashima [8] have been (and are) investigating scaling parameters for reducing the Tosi–Fumi potential function [9, 10] and have advanced a corresponding states-based viscosity–temperature correlation equation for the alkali metal fluorides. Young and O'Connell [11], from more phenomenological considerations of the corresponding-states principle, have advanced predictive correlations for a series of transport properties and, specifically, for molten salt systems. The latter approach is being reexamined in our present studies, and the results for single salts in the molten state are reported in this paper herewith.

3. CRITICALLY EVALUATED MOLTEN SALTS DATA BASE

Critical data evaluation studies at RPI for molten salts are part of the National Standards Reference Data System Program under the National Bureau of Standards (NBS-NSRDS). Results for the four most widely used properties, *viz.*, density, surface tension, viscosity, and electrical conductance, have been published as a series since 1968 [12–20], and the complete data base, upgraded and updated to March 1988 is currently in press [21]. The latter has been used as data source in the present communication. In the course of these studies and in parallel, a project was undertaken in 1973 that has become known as the Molten Salts Standards Program [22]. In cooperation with laboratories in Czechoslovakia, DDR-Germany, Japan, Norway, Poland, Rumania, and the United States, measurements were undertaken (over a 5-year period), on round-robin samples of two salts, NaCl and KNO_3, both of Standards Quality purity. In addition to firming up the data sets for these two salts as calibration-quality accuracies, insights were gained on the various measurement techniques through intercomparisons. The results have been used to provide guidance throughout our critical evaluations in matters of value judgments.

4. CORRESPONDING-STATES CORRELATIONS AND PREDICTIVE CALCULATIONS

The underlying approach of Young and O'Connell [11] for the corresponding-states equations for the temperature dependence of density, and the transport properties of molten salts, briefly, is as follows. An

inherent assumption is that the liquid state follows conformal solution theory, and this seems valid to a remarkable degree for fully ionized salts in which the configurational interactions do not lead to the formation of "new" species, i.e., new compounds.

4.1. Reduced Molar Volume–Reduced Temperature Relation

For such fluids (above) it has been shown [23] that the reduced equation of state for all substances under conditions of the same number density may be expressed as:

$$v/v^* = \tilde{v}(T/T^*, P/P^*) \qquad (1)$$

where the properties with asterisk superscripts are related to the potential parameters for the configurational interactions in conformable systems. For the majority of molten salts the pressure dependence of density may be assumed as negligible under ambient conditions, and this equation then simplifies to

$$\tilde{v} = \tilde{v}(\tilde{T}) \qquad (2)$$

where $\tilde{v}$ and $\tilde{T}$, the reduced variables, equal (v/v^*) and (T/T^*), respectively. The product of temperature and expansivity may thus be expressed in reduced variables as

$$(T/v)(\partial v/\partial T)_p = (\tilde{T}/\tilde{v})(\partial \tilde{v}/\partial \tilde{T})_{\tilde{p}} = f(\tilde{T}) \qquad (3)$$

i.e., as a universal function of reduced temperature. It follows that the liquids are in identical corresponding states when they are at identical values of the function: $f(\tilde{T})$. For simple liquids, Renon et al. [4] proposed that the value of $f(\tilde{T})$ should be such that it places the corresponding state within the liquid ranges of all the fluids.

The values

$$f(\tilde{T}) = 0.4, \qquad \text{at } \tilde{T} = 1 \text{ at this point}$$

have thus been proposed by Renon et al. to define the corresponding state conditions. The same conditions were assumed by Young and O'Connell and also in the present work.

Values for the characteristic temperatures, volumes, and viscosity have been calculated, accordingly, from the molten salts data base [12–22] for a representative series of salts. The experimental densities and viscosities for this series fall generally within the accuracy limits of ± 1.5 and $\pm 3\%$, respectively. The results are shown in Table I. Inspection of (T_m/T^*)

Table I. Characteristic State Data: Molten Salts[a]

Salt	T^*	v^*	T_m/T^*	η^*
CsBr	991	89.97	0.917	1.366
CsCl	1011	62.55	0.908	1.187
CsF	1093	43.42	0.873	1.167
CsI	1027	85.47	0.870	1.101
CsNO$_3$	887	75.36	0.778	—
Cs$_2$CO$_3$	2025	112.99	—	0.644
KBr	1024	56.32	0.983	1.170
KCl	1047	48.87	0.998	1.097
KF	1161	30.74	0.972	1.255
KI	1004	69.18	0.954	1.195
KNO$_3$	911	61.37	0.670	0.887
K$_2$CO$_3$	1560	80.14	0.749	1.508
KOH	1308	39.02	0.484	—
LiBr	1344	39.68	0.610	0.657
LiCl	1244	31.50	0.710	0.689
LiF	1374	15.40	0.741	1.192
LiI	1181	48.43	0.611	0.744
LiNO$_3$	1082	46.69	0.487	—
LiOH	1074	19.52	0.684	—
Li$_2$CO$_3$	1688	46.97	0.597	1.198
NaBr	1110	43.58	0.919	0.950
NaCl	1126	38.25	0.953	0.932
NaF	1238	21.33	1.024	1.567
NaI	1092	57.85	0.856	0.814
NaNO$_3$	927	51.30	0.629	—
NaOH	1235	27.08	0.478	—
Na$_2$CO$_3$	1579	59.85	0.713	1.703
RbBr	997	61.94	0.956	1.382
RbCl	1010	54.23	0.980	1.302
RbF	1118	36.62	0.937	1.330
RbI	987	93.07	0.925	1.272
RbNO$_3$	839	65.83	0.702	—
Rb$_2$CO$_3$	1583	91.13	—	1.362
MgCl$_2$	1869	67.46	0.528	0.674
CaCl$_2$	1708	61.52	0.617	0.866
SrCl$_2$	1675	65.38	0.685	1.183
BaCl$_2$	1684	72.63	0.733	1.345

[a] Units: T^*, T (K); v^* (cm$^3 \cdot$ mol^{-1}); η^* (mN $\cdot$ s $\cdot$ m^{-2}).
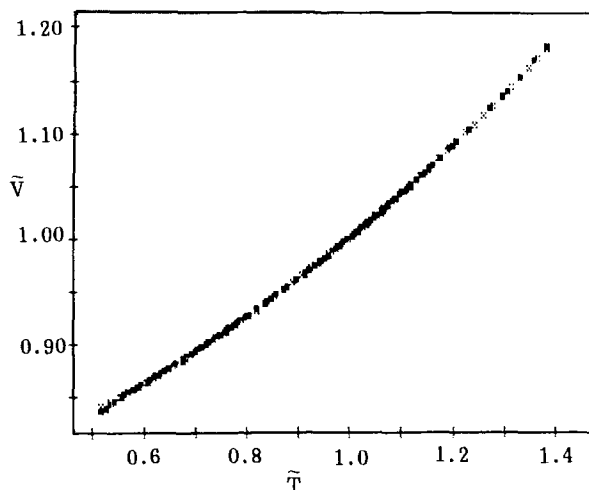
Fig. 1. Molten salts molar volume–temperature data: corresponding-states correlation.

confirms that the corresponding states fall within the liquid ranges for this series of salts; NaF appears to be an exception, but this was not pursued further for the present.

The reduced molar volume–reduced temperature data set for 37 salts (300 points) is shown graphically in Fig. 1. The results are expressed by

$$\tilde{v} = 0.7452 + 0.1049\tilde{T} + 0.1502\tilde{T}^2 \qquad (4)$$

for this correlation, with the standard error of estimate (SEE) = 8.61×10^{-4}. The values of the parameters in Eq. (4) differ only modestly from the results of the analysis by Young and O'Connell [11], with the shifts being to lower values.

4.2. Reduced Viscosity–Reduced Temperature Correlation

The extension of the preceding approach by Young and O'Connell to transport properties, such as viscosity, involves the empirical assumption that a similar relation [like Eq. (4)] also holds for the transport properties.

A reduced viscosity–reduced temperature data set (150 data points) for 26 of the salts listed in Table I was compiled and investigated accordingly. The correlation for the reduced properties is shown in Fig. 2 and leads to the equation

$$\ln \tilde{\eta} = -1.998 + 2.065/\tilde{T} - 0.0573\tilde{T}^8 \qquad (5)$$
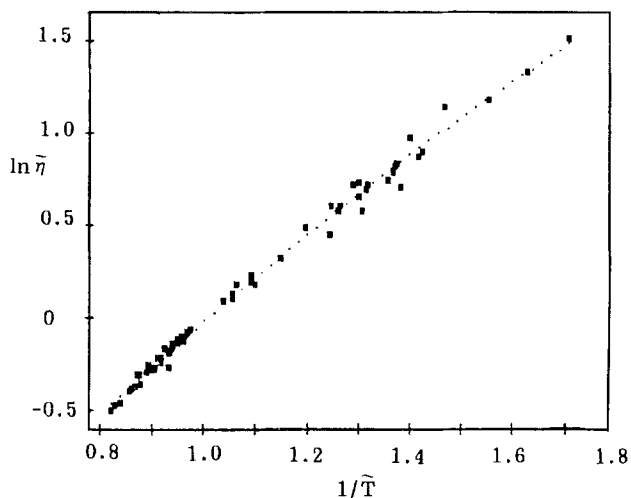
Fig. 2. Molten salts viscosity–temperature data: corresponding-states correlation.

for a least-squares analysis, with $SEE = 5.42 \times 10^{-2}$, and for the range $0.5 < \tilde{T} < 1.15$. The equation is of the same format as found by Young and O'Connell, but the values of the parameters have shifted (modestly) to lower values.

The data for some 2–1- and 1–2-type salts (i.e., $MgCl_2$) and for some lithium 1–1 salts (such as LiI) were dropped from the correlation data set because of the large scattering. It should also be noted that the data for molten fluorides are found to fall outside the above limits for $\tilde{T}$.

For predictive calculations, one notes that the above relation [Eq. (5)] may be expressed as

$$\eta = (\eta^*)\, f(T/T^*) \tag{6}$$

and that once the values of η^* and T^* have been determined, a simple equation relating η and T has been gained which is well suited for predictive calculations.

To find the values for the two characteristic parameters, one needs, for each salt, a knowledge of

   (i)   density data (sufficient to establish the value of T^*) and

  (ii)   a single (viscosity, temperature) data-point pair (i.e., one value of the viscosity).

4.3. Predictive Calculations

The series of salts, together with the properties parameters, is shown in Table II. The NSRDS data compilations were used as sources for the densities and the one measured value of viscosity for each salt, unless otherwise noted. The NSRDS compilations have detailed supporting literature references; only citations to the additional studies have been added in the present work. The quality of the measured viscosity data point was linked to the recent experimental work of Oye et al. (alkali and alkaline earth metal chlorides [24, 25, 27]) and Ejima et al. (alkali metal bromides, iodides, and carbonates [26, 28, 30]), accordingly. The accuracy limits of this data point are as follows: alkali metal chlorides, $\pm 1\%$; alkali metal bromides and iodides, $\pm 1.5\%$; alkaline earth chlorides, $\pm 1\%$; and alkali metal carbonates, $\pm 3\%$. For molten NaCl and KNO_3, the accuracy limits are those of the Molten Salts Standards Program, viz., ± 0.8 and $\pm 2\%$,

Table II. Data and Source References for Predictive Calculations

Salt	Density Ref. Nos.	Measured viscosity point		
		T (K)	$(mN \cdot s \cdot m^{-2})$	Ref. Nos.
NaCl	21, 22	1076.7	1.038	12, 21, 22, 24
KNO_3	21, 22	751.1	1.488	12, 21
LiCl	12, 22	1031.7	1.007	12, 25
KCl	12, 22	1130.0	0.887	25
RbCl	12, 22	988.0	1.391	12, 25
CsCl	12, 22	979.2	1.301	12, 25
LiBr	12, 22	854.6	1.589	17, 26
NaBr	12, 22	1083.0	1.005	26
KBr	12, 22	1122.0	0.920	12, 26
RbBr	12, 22	1063.0	1.157	12, 26
CsBr	12, 22	1032.0	1.219	26
LiI	12, 22	851.1	1.474	12, 26
NaI	12, 22	1024.2	0.935	26
KI	12, 22	1058.0	1.055	26
RbI	12, 22	1015.0	1.183	26
CsI	12, 22	997.0	1.197	26
$MgCl_2$	12, 22	1114.1	1.651	17, 27
$CaCl_2$	12, 22	1056.5	3.234	16, 27
$SrCl_2$	12, 22	1147.3	3.747	27
$BaCl_2$	12, 22	1280.0	3.277	27
Li_2CO_3	12, 22	1054.3	4.542	12, 28, 30
Na_2CO_3	12, 22	1181.7	2.754	12, 28–30
K_2CO_3	12, 22	1200.4	2.712	12, 28, 30

respectively [21, 22, 24]. The selection of the viscosity point was not purely arbitrary; it was guided by a comparison of the earlier studies. If the comparisons led to a point of intersection, and if this point was also in the liquid range, this (i.e., the intersecton or crossover point) was selected for the calculations. When an intersection was not found, i.e., due to parallel or slowly converging curves, the approximate midpoint of the experimental data set was selected.

5. RESULTS AND DISCUSSION

In Table III, comparisons of the calculations and measurements are given, together with the viscosity equations of the experimental studies from which the "seed" values were selected [24–27, 29, 30]. The equations

Table III. Comparison of Calculated with Measured Values:
% Departure = [(Calc. − Measured)/Measured] %

Salt	$\eta = A \exp(E/RT)$			Comparison			
	A	E (J·mol^{-1}·K^{-1})	T range (K)	T_1	% dep.	T_2	% dep.
NaCl	0.08927	21960.1	1080–1210	1080	−0.04	1120	−0.4
KNO$_3$	0.07737	18468.5	615– 760	700	−1.9	750	−0.15
LiCl	0.10852	19111.4	894–1113	900	6.8	1100	−1.0
KCl	0.06166	25047.3	1111–1162	1120	0.3	1160	−0.8
RbCl	0.06783	24805.2	1023–1172	1050	1.6	1150	0.4
CsCl	0.07148	23619.4	934–1072	950	−1.0	1050	0.9
LiBr	0.14030	17246.2	823–1082	850	0.5	1050	−17.0
NaBr	0.10340	20478.3	1022–1192	1050	0.7	1150	−1.8
KBr	0.07370	23543.3	1011–1194	1030	1.3	1180	−3.4
RbBr	0.08060	23550.3	971–1197	1000	−0.08	1150	−4.0
CsBr	0.08470	22920,3	912–1192	950	−1.4	1150	−4.5
LiI	0.12650	17386.2	742–1028	730	7.9	1000	−9.0
NaI	0.09940	19095.3	941–1117	1000	0.7	1100	−3.3
KI	0.10230	20521.3	965–1193	1000	1.8	1150	−6.2
RbI	0.07640	23081.3	934–1194	1000	0.3	1150	−5.1
CsI	0.07720	22701.3	917–1198	1000	0.3	1150	−3.2
MgCl$_2$	0.17939	20558.7	993–1170	1000	18.0	1150	−4.4
CaCl$_2$	0.10215	30351.0	980–1240	1000	0.4	1200	−0.9
SrCl$_2$	0.09638	34917.8	1150–1300	1180	1.1	1280	4.6
BaCl$_2$	0.07993	39521.6	1210–1320	1250	−1.9	1300	1.2
Li$_2$CO$_3$	0.08660	36862.5	1019–1197	1050	0.5	1150	−4.7
Na$_2$CO$_3$	0.18937	28834.1	1134–1234	1150	0.5	1200	0.1
K$_2$CO$_3$	0.18751	27037.9	1186–1234	1190	0.13	1230	0.08

are the recommended values in the upgraded NSRDS molten salts data base [21]. The two comparison temperatures bridge the seed value.

Inspection shows that the calculated results for NaCl and KNO_3 are in close accord with the measurements, both in the temperature dependence and in the numerical values. In Fig. 3, the comparison is shown graphically. The departures are somewhat larger over a broader temperature range, but it appears that this may be due largely to differences in the analytical nature of the experimental and calculated equations. For example, it can be shown that the calculated equation can be converted, as a good first approximation, to the simple exponential format of the experimental equation for values of $\tilde{T}$ significantly less than 1.0.

The results for the other salts (Table III) are, in general, in accord with the results for the two model systems. The underlying assumption of this predictive method, namely, that of conformal solution behavior, thus receives support from this study. Exceptions appear to be LiCl, LiBr, LiI, and $MgCl_2$; the departures are somewhat larger. Li_2CO_3, in contrast, appears "well behaved." The confidence level in the measurements is high.
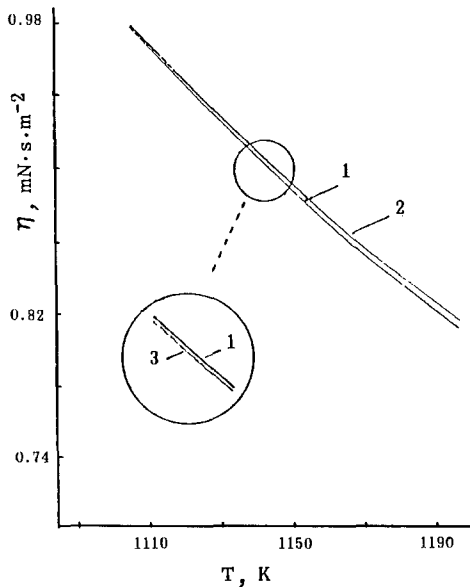

Fig. 3. Test of the predictive correlation with NaCl viscosities. Curve 1, Molten Salts Standards Program (damped oscillational technique [21, 24]); curve 2, capillary technique [26]; curve 3 (inset), from the predictive calculations.

The larger departures (16–25%) suggest failure of the behavioral model (i.e., that these are due to onsets of interactions leading to deviations from conformal behavior) in these melts.

    In data evaluations work, a problem one frequently encounters is illustrated in Fig. 4, where the results of two viscosity studies for Na_2CO_3 [12, 28] are graphed, together with the calculated results of the present work. Judgment between the results of Vorobev et al. [28] and those of Janz and Saegusa [12, 31], without the predictive calculations and the further support of the later measurements of Ejima et al. [29, 30], is difficult at best and rests on comparisons of measurements methods, experimental assemblies, and working equations, as well as matters of sample pretreatments and purities. More could be listed. Details like this are all too frequently minimal or completely lacking in the published papers. Inspection shows that the results of Vorobev et al. are in close accord with
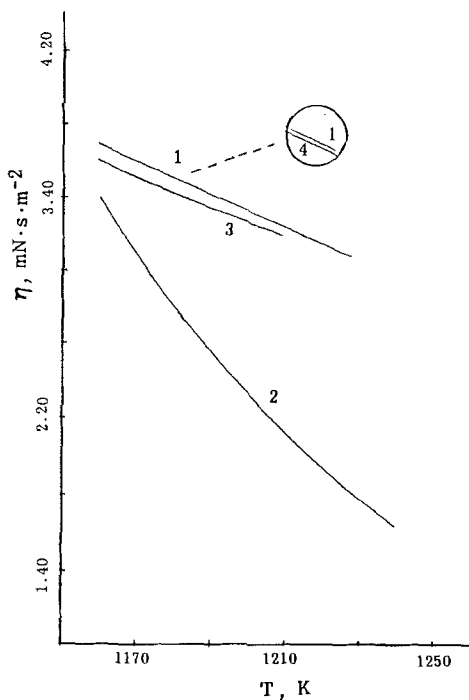

Fig. 4. Na_2CO_3 viscosity studies. Curve 1, measurements of Vorobev et al. (1965) [28]; curve 2, measurements of Janz and Saegusa (1963) [12, 31]; curve 3, from the predictive calculations; curve 4 (inset), measurements of Ejima et al. [29, 30].

the calculated results. Furthermore the latter are firmly supported by the latest measurements (Table III, carbonates). The predictive calculations thus provide an additional touchstone for reference in matters of quality judgments. In the same study, Vorobev et al. [28] investigated the viscosities of binary mixtures of the lithium, sodium, and potassium carbonates. It follows that these can also be recommended with improved confidence levels.

The selection of a corresponding state that falls in the liquid range, rather than at the melting point of the salt, and the underlying assumption that the configurational interactions are conformable in this set of molten salts receive support from the preceding results. With due attention to the assumptions and to the quality of measured data points, this predictive approach appears promising as an assist to value judgments in this area of molten salts data studies.

ACKNOWLEDGMENT

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