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A modified rough hard-sphere model for the viscosity of molten salts

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ABSTRACT

We present a new model for the viscosity of molten salts based on the modified Rough-Hard-Sphere (RHS) scheme of DiGuilio and Teja. The model employs the properties of argon to obtain smooth-hard-sphere (SHS) viscosity, and the melting points of the molten salts as characteristic parameters. The performance of the model to correlate/predict the viscosities of 38 molten salts is examined in this work. Our results show that the viscosities of these molten salts can be correlated with an AAD (average absolute deviation between calculated and experimental values) of 1.50% using one adjustable parameter for each salt. In addition, values of the adjustable parameter exhibit regular trends with the melting point of the salt for a series of salts with a common anion.

1. Introduction

Molten salts have attracted much interest lately because of their potential application as high temperature thermal energy storage materials in concentrated solar power (CSP) plants [1]. They are also of interest in applications involving molten carbonate fuel cells [2], nuclear reactors [3], and refractory metals [4]. The heat transfer efficiency of equipment in these applications is significantly affected by the transport properties of the molten salt, particularly its viscosity and thermal conductivity. As a result, considerable effort has been devoted to the measurement of the transport properties of salts of interest in these applications. However, the data are sometimes contradictory (especially in the case of the thermal conductivity), and often do not extend to the high temperatures of interest in CSP applications [5]. It is therefore important to develop models to analyze, correlate and extrapolate/predict molten salt transport properties.

The most successful transport property models for molten salts have employed either the corresponding states principle or the rough-hard-sphere theory. Corresponding states viscosity-temperature equations for alkali halides have been reported by Abe and Nagashima [6] with scaling parameters based on the Tosi-Fumi potential function. Young and O'Connell [7] have also presented a corresponding states correlation with scaling parameters based on an arbitrary point on the saturation curve, whereas Janz et al. [8] have used model systems (NaCl and KNO_3) to develop their equation for the viscosity of specific salts.

Rough-hard-sphere approaches have achieved considerable success in modeling the transport properties of liquids (Chandler [9], Assael et al. [10–15], Ciotta et al. [16], Teja et al. [17–19]). DiGuilio and Teja [20] extended the rough-hard-sphere approach to correlate/predict the thermal conductivity of monovalent molten salts by using one molten salt as the reference fluid and the melting point of the salt to define its RHS parameters. The approach was further extended by Hossain et al. [21] to both monovalent and multivalent molten salts. In the present work, we extend the work of DiGuilio and Teja to the viscosity of molten salts.

2. Development of the model

Chandler [9] showed that the viscosity of rough hard spheres (RHS) can be obtained from that of smooth hard spheres (SHS) by introducing a translational-rotational coupling parameter C_η as follows:

$$\eta^*_{RHS} = C_\eta \, \eta^*_{SHS} \tag{1}$$

The coupling parameter C_η in Equation (1) (also called the roughness parameter by Assael et al. [10–15]) accounts for coupling between translational and rotational contributions to the transport properties of spheres. In addition, the reduced viscosity in Equation (1) was expressed as:

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$$\eta^*_{RHS} = 6.035 \times 10^8 \left(\frac{1}{MRT}\right)^{1/2} \eta \; V^{2/3} \tag{2}$$

where T is the temperature (K), M is the molecular weight ($kg \cdot mol^{-1}$), R is the gas constant (=8.3141 $J \cdot mol^{-1} \cdot K^{-1}$), V is the molar volume ($m^3 \cdot mol^{-1}$), and η is the viscosity (Pa·s).

Subsequently, Assael et al. [10–15] expressed the reduced viscosity of smooth hard spheres according to:

$$\log \eta^*_{SHS} = F_\eta \; [V/V_0] \tag{3}$$

where V_0 is the molar volume at closest packing, given by $V_0 = N_A\sigma^3/\sqrt{2}$ for spheres of diameter σ. Analogous equations can also be written for the thermal conductivity as follows:

$$\lambda^*_{RHS} = C_\lambda \; \lambda^*_{SHS} \tag{4}$$

$$\lambda^*_{RHS} = 1.936 \times 10^7 \left(\frac{M}{RT}\right)^{1/2} \lambda \; V^{2/3} \tag{5}$$

and

$$\log \lambda^*_{SHS} = F_\lambda \; [V/V_0] \tag{6}$$

where again, T is the temperature (K), M is the molecular weight ($kg \cdot mol^{-1}$), R is the gas constant (= 8.3141 $J \cdot mol^{-1} \cdot K^{-1}$), V is the molar volume ($m^3 \cdot mol^{-1}$), and λ is the thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$).

In the case of molten salts, DiGuilio and Teja [20] replaced the molar volume at closest packing in Equation (6) by the molar volume of the solid salt at its melting point V_s. In addition, a volume translation ($V - V_m$) was used to shift the origin of the function F_λ to the melting point. Thus Equation (6) was replaced with:

Table 1
Viscosity data references for molten salts.

Molten salt	# Data	T range (K)	Viscometer	Uncertainty	Ref
LiCl	15	886–1169	Capillary	0.7%	[23]
NaCl	12	1077–1180	Capillary	0.7%	[23]
KCl	15	1050–1190	Capillary	0.7%	[23]
RbCl	16	1000–1182	Capillary	0.7%	[23]
CsCl	17	933–1183	Capillary	0.7%	[23]
LiBr	18	823–1081	Capillary	0.7%	[24]
NaBr	14	1022–1192	Capillary	0.7%	[24]
KBr	19	1010–1194	Capillary	0.7%	[24]
RbBr	13	971–1197	Capillary	0.7%	[24]
CsBr	15	911–1192	Capillary	0.7%	[24]
LiI	20	742–1028	Capillary	0.7%	[24]
NaI	18	940–1117	Capillary	0.7%	[24]
KI	16	965–1193	Capillary	0.7%	[24]
RbI	14	933–1194	Capillary	0.7%	[24]
CsI	15	916–1198	Capillary	0.7%	[24]
LiF	11	1128–1341	Oscillating	2%	[25]
NaF	9	1277–1364	Oscillating	2%	[25]
KF	11	1141–1328	Oscillating	2%	[25]
RbF	9	1078–1274	Oscillating	2%	[25]
CsF	11	981–1281	Oscillating	2%	[25]
$LiNO_3$	13	550–670	–	–	[26]
$NaNO_3$	33	590–750	Oscillating	2.1%	[27]
KNO_3	14	615–760	–	–	[28]
$RbNO_3$	8	600–670	–	–	[26]
$CsNO_3$	17	695–770	–	–	[26]
MgF_2	17	1514–1853	Oscillating	1%	[29]
CaF_2	21	1703–1868	Oscillating	1%	[29]
SrF_2	16	1750–1865	Oscillating	1%	[29]
BaF_2	15	1620–1880	Oscillating	1%	[29]
$MgCl_2$	32	993–1173	Oscillating	0.3%	[30]
$CaCl_2$	39	1060–1239	Oscillating	0.3%	[30]
$SrCl_2$	33	1152–1318	Oscillating	0.3%	[30]
$BaCl_2$	37	1239–1372	Oscillating	0.3%	[30]
$CeCl_3$	52	1090–1176	Capillary	–	[31]
$NdCl_3$	49	1024–1151	Capillary	–	[31]
$SmCl_3$	54	948–1094	Capillary	–	[31]
$DyCl_3$	72	992–1179	Capillary	–	[31]
$ErCl_3$	24	1066–1135	Capillary	–	[31]

Table 2
Molecular weight, melting temperature, and density for all molten salts studied.

Salt	M_w ($g \cdot mol^{-1}$)	T_m (K)	Density ($g \cdot cm^{-3}$)
LiCl	42.394	883	$\rho = 1.8842 - 4.328 \times 10^{-4}T$
NaCl	58.443	1074	$\rho = 2.1393 - 5.430 \times 10^{-4}T$
KCl	74.551	1049	$\rho = 2.1359 - 5.831 \times 10^{-4}T$
RbCl	120.921	988	$\rho = 3.1210 - 8.832 \times 10^{-4}T$
CsCl	168.358	919	$\rho = 3.7692 - 1.065 \times 10^{-3}T$
LiBr	86.845	820	$\rho = 3.0658 - 6.520 \times 10^{-4}T$
NaBr	102.894	1020	$\rho = 3.1748 - 8.169 \times 10^{-4}T$
KBr	119.002	1007	$\rho = 2.9583 - 8.253 \times 10^{-4}T$
RbBr	165.372	955	$\rho = 3.7390 - 1.0718 \times 10^{-3}T$
CsBr	212.809	909	$\rho = 4.2449 - 1.2234 \times 10^{-3}T$
LiI	133.845	742	$\rho = 3.7902 - 9.176 \times 10^{-4}T$
NaI	149.894	933	$\rho = 3.6274 - 9.491 \times 10^{-4}T$
KI	166.002	954	$\rho = 3.3594 - 9.557 \times 10^{-4}T$
RbI	212.372	920	$\rho = 3.9499 - 1.1435 \times 10^{-3}T$
CsI	259.81	899	$\rho = 4.2410 - 1.1834 \times 10^{-3}T$
LiF	25.939	1120	$\rho = 2.3768 - 4.902 \times 10^{-4}T$
NaF	41.988	1268	$\rho = 2.6550 - 5.600 \times 10^{-4}T$
KF	58.097	1131	$\rho = 2.6464 - 6.515 \times 10^{-4}T$
RbF	104.466	1068	$\rho = 3.9953 - 1.021 \times 10^{-3}T$
CsF	151.904	976	$\rho = 4.8985 - 1.2806 \times 10^{-3}T$
$LiNO_3$	68.946	525	$\rho = 2.0680 - 5.460 \times 10^{-4}T$
$NaNO_3$	84.995	580	$\rho = 2.320 - 7.150 \times 10^{-4}T$
KNO_3	101.103	607	$\rho = 2.315 - 7.290 \times 10^{-4}T$
$RbNO_3$	147.473	583	$\rho = 3.049 - 9.720 \times 10^{-4}T$
$CsNO_3$	194.910	687	$\rho = 3.6206 - 1.1661 \times 10^{-3}T$
MgF_2	62.302	1536	$\rho = 3.235 - 5.240 \times 10^{-4}T$
CaF_2	78.075	1691	$\rho = 3.179 - 3.910 \times 10^{-4}T$
SrF_2	125.62	1673	$\rho = 4.784 - 7.510 \times 10^{-4}T$
BaF_2	175.324	1593	$\rho = 5.775 - 9.990 \times 10^{-4}T$
$MgCl_2$	95.211	981	$\rho = 1.976 - 3.020 \times 10^{-4}T$
$CaCl_2$	110.984	1046	$\rho = 2.5261 - 4.225 \times 10^{-4}T$
$SrCl_2$	158.53	1146	$\rho = 3.3896 - 5.781 \times 10^{-4}T$
$BaCl_2$	208.233	1235	$\rho = 4.0152 - 6.813 \times 10^{-4}T$
$CeCl_3$	246.475	1095	$\rho = 4.248 - 9.20 \times 10^{-4}T$
$NdCl_3$	250.601	1031	$\rho = 4.2379 - 8.6745 \times 10^{-4}T$
$SmCl_3$	256.76	955	$\rho = 4.2048 - 7.472 \times 10^{-4}T$
$DyCl_3$	268.859	991	$\rho = 4.3442 - 7.4828 \times 10^{-4}T$
$ErCl_3$	273.618	1049	$\rho = 4.4406 - 7.9911 \times 10^{-4}T$

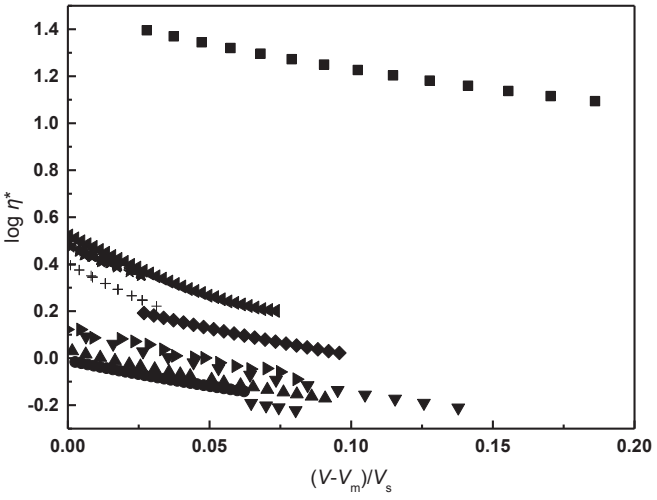

Fig. 1. log η^* as a function of $(V - V_m)/V_s$ for argon and molten salts. ■ Ar; ● NaCl; ▲ KBr; ▼ RbI; ◆ LiF; ◂ $NaNO_3$; ▸ MgF_2; + $BaCl_2$; ★ $CeCl_3$.