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The fluidity of molten salts re-examined

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ABSTRACT

The fluidity, Φ, of molten salts is re-examined with critically compiled data applicable to 75 salts of various charge types. Various theoretical approaches, based on the corresponding states principle applicable to molten salts, are briefly presented. They are compared with the much simpler approach of Hildebrand and Lamoreaux: $\Phi = -B + (B/V_0)V$ that relates the (temperature dependent) fluidity to the (temperature dependent) molar volume V of the molten salt. This approach yields at the corresponding temperature of 1.1 T_m the B parameters that are linearly related to the cohesive energy and the V_0 parameters that are 87% of the molar volume, signifying the absence of free volume.

1. Introduction

The fluidity of a liquid is the reciprocal of its dynamic viscosity: $\Phi = \eta^{-1}$ and is measured in s mPa^{-1}. The viscosity of many molten salts obeys the Arrhenius expression, hence their fluidity does so too:

$$\Phi = \Phi_0 \exp \frac{E_\Phi}{RT} \quad (1)$$

where $E_\Phi = -E_\eta$, the latter being the activation energy for the viscous flow. Some molten salts, the ions of which are either associating to a network (eventually glass-forming at lowered temperature) or suffer from hindered rotation in the melt follow a non-Arrhenius temperature dependence [1]. The fluidity of such salts may be described by the Vogel–Tammann–Fulcher (VTF) expression:

$$\Phi = \Phi_0 \exp \frac{K}{T - T_0} \quad (2)$$

or its modification, where $\Phi_0 = \Phi_0' T^{1/2}$. Further expressions are those of Litovits [2], where in Eq. (1) T in the denominator of the exponent is replaced by T^3 or that of Ghatee et al. [3]:

$$\Phi^{0.3} = a + bT \quad (3)$$

However, a more-or-less-forgotten expression, originally proposed by Hildebrand and Lamoreaux [4,5] for various liquids and taken up by Chhabra and Hunter [6] specifically for molten salts, relates their fluidity to their (temperature dependent) molar volumes:

$$\Phi = -B + \frac{B}{V_0} V \quad (4)$$

The latter authors [6] did not have the benefit of the critical compilation of density and viscosity data for molten salts by Janz [7], hence some of their calculated values are inaccurate. The B parameters are loosely related to the forces between the constituent particles and the V_0 parameters to the absence of free volumes in the liquids.

In the present paper the linearity of Eq. (4) for molten salts is confirmed and the parameters B and V_0 for 75 molten salts of the 1:1, 2:1, and 1:2 charge types are derived. The salts examined are limited by the availability of the viscosity and density data ([7] and a few other publications) and the requirement that the salts are ionic to an appreciable degree. The B values are related to two quantities describing the inter-ionic interactions in the molten salts: the cohesive energy, ce, and the molar heat capacity at constant pressure, C_P.

2. Results

Values of the dynamic viscosity $\eta = \eta_0 \exp(E_\eta/RT)$ and of the density $\rho = a - bT$ are from Janz [7] unless otherwise noted, and are leading to the corresponding $\Phi(T) = \eta(T)^{-1}$ and $V(T) = M/\rho(T)$ values, where M is the molar mass of the molten salt. These data, required for the application of Eq. (4), are valid for the temperature ranges quoted in [7]. Fig. 1 shows some representative linear dependencies of Φ on V. In all the 75 molten salts examined the linear correlation coefficients of the plots of Eq. (4) are ≥0.995.

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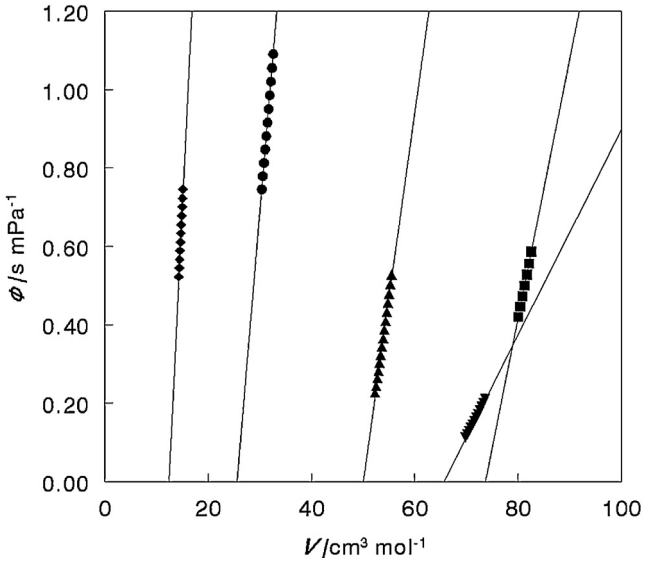

Fig. 1. The fluidities Φ of some molten salts plotted against their molar volumes, limited to the temperature ranges where the viscosity data are available [7]. The linear correlation coefficients are: LiF (♦) 0.99999, KF (●) 0.99997, $CaCl_2$ (▲) 0.99900, Na_2SO_4 (▼) 0.99920, and $CsNO_3$ (■) 0.99972.

The derived B and V_0 values are independent of the temperature and are recorded in Table 1. Also listed there are the ce and C_P values of the molten salts, taken from the author's publications [8–10], noting that these values are valid for the corresponding temperature 1.1 T_m, at which molten salts ought to be compared.

The B value for $MgBr_2$ listed in Table 1 is much out of line from the other values and the viscosity expression in [7] on which it is based, $\eta = 0.003409\exp(60213.4/RT)$, has numerical coefficients also very different from other such expressions given there. It is concluded that this expression and the derived B value must be incorrect. A similar objection is raised against the viscosity data of $BiCl_3$ in [7], yielding a B value much smaller than expected.

3. Discussion

Fully ionized molten salts are conformal fluids in that they obey a universal potential function, namely the widely accepted Tosi-Fumi one [11] that yields the distance, σ, and energy, ε, parameters of the pair potential. Accepting this concept, Young and O'Connell [12] presented an empirical corresponding state correlation of the viscosity of molten 1:1 alkali metal salts that in the final reckoning relates the fluidity to the molar volume. Their expression is rewritten as:

$$\ln\frac{\Phi}{\Phi^*} = 2.11 - 2.17\frac{T^*}{T} + 0.06\left(\frac{T}{T^*}\right)^8 \quad (5)$$

where T^* is a characteristic temperature defined as $T^* = 0.4/\alpha_P$, α_P being the isobaric expansibility. The characteristic fluidity Φ^* is obtained from:

$$\Phi^* = A_\Phi V^{*2/3}(2\mu T^*)^{-1/2} \quad (6)$$

with $A_\Phi = 13.8$, $\mu = M_+M_-/(M_+ + M_-)$, the M being the molar masses of the cation (+) and anion (−), and the characteristic volumes V^* being given by:

$$\frac{V}{V^*} = 0.7458 + 0.1048\frac{T}{T^*} + 0.1458\left(\frac{T}{T^*}\right)^2 \quad (7)$$

The root mean square deviation of the calculated from the experimental viscosities (also fluidities) was 3.3%.

Table 1
The B and V_0 parameters of Eq. (4) for molten salts and their cohesive energy density ce and heat capacity C_P at the corresponding temperature 1.1 T_m. (The V_0 values in parentheses are from [4].).

Salt	B (s mPa^{-1})	V_0 (cm^3 mol^{-1})	ce (kJ mol^{-1})	C_P (J K^{-1} mol^{-1})
LiF	3.36	12.4	956	64.2
LiCl	6.52	25.4 (26.7) *22.4*	825	64.0
LiBr	6.24	31.8 (32.3) *28.0*	735	65.3
LiI	5.96	40.5 (40.0)	681	63.2
$LiNO_3$	7.21	38.2 (38.0) *40.3*	790	112.5
$LiClO_3$	2.65	44.2		122.2
$LiClO_4$	4.60	51.5	700	161.1
NaOH	7.37	21.9	898	87.1
NaF	3.68	18.2	891	70.5
NaCl	5.00	31.5 (34.5) *34.2*	694	67.8
NaBr	4.73	37.1 (37.4) *36.8*	665	62.3
NaI	5.49	47.2 (49.0) *53.0*	613	64.9
$NaNO_2$	5.83	36.0	758	116.7
$NaNO_3$	6.50	41.7 *54.6*	693	136.8
NaSCN	3.78	42.1	723	
$NaClO_3$	3.48	49.3	780	133.9
$NaBF_4$	4.98	52.2	669	165.4
KOH	6.75	30.6	801	83.1
KF	3.96	26.6	725	66.9
KCl	5.56	41.5 (42.6) *46.2*	622	73.6
KBr	4.93	48.0 (47.0) *53.0*	594	69.9
KI	4.22	57.7 (58.6) *66.8*	558	72.4
KNO_2	2.73	42.1	711	
KNO_3	5.22	50.9 (50.9) *69.2*	617	123.4
KSCN	3.95	46.2	583	
RbF	3.87	30.7	595	59.4
RbCl	4.91	46.9 (51.4)	614	64.0
RbBr	4.42	53.2 (51.4)	589	66.9
RbI	4.97	65.0 (63.6)	560	66.5
$RbNO_3$	3.85	55.8	613	
CsF	4.34	35.2	674	74.1
CsCl	5.00	53.5 (57.7) *63.0*	590	74.4
CsBr	4.48	60.3 *68.6*	563	77.4
CsI	5.35	73.5 (73.4)	531	72.4
$CsNO_3$	4.89	73.6	574	136.0
$AgNO_3$	5.66	48.7	772	139.1
$TlNO_3$	6.17	52.2	699	130.3
CuCl	7.51	26.1	1005	66.9
AgCl	4.74	30.4	917	61.2
AgBr	3.97	35.0	904	59.3
AgI	5.77	44.6	890	58.6
TlCl	3.00	40.9	748	59.4
TlBr	3.93	45.7	728	77.9
TlI	4.06	49.3	699	72.0
Li_2CO_3	3.65	39.0	2494	142.8
Li_2SO_4	3.86	53.0	2158	207.9
Li_2MoO_4	2.86	58.2	1999	215.1
Li_2WO_4	3.90	60.4	2000	205.0
Na_2CO_3	2.65	49.3	2270	189.5
Na_2SO_4	1.73	65.7	1758	197.4
Na_2MoO_4	3.10	70.0	1983	213.0
Na_2WO_4	3.73	73.4	1987	209.2
K_2CO_3	2.96	65.5	2045	183.8
K_2MoO_4	5.94	87.5	1635	
K_2WO_4	2.09	95.0	1941	213.4
Rb_2CO_3	3.17	74.2	2030	
Cs_2CO_3	3.74	86.6	1949	
$K_2Cr_2O_7$	2.05	124.3	1639	415.9
$MgCl_2$	5.64	52.2	2467	92.5
$MgBr_2$	14.44?	69.9	2433	104.6
$CaCl_2$	4.62	50.0	2258	106.7
$SrCl_2$	3.92	54.2	2134	104.6
$BaCl_2$	3.49	61.0	2035	108.8
$ZnCl_2$	2.38	55.1	2693	100.8
$ZnBr_2$	3.47	66.1	2637	113.8
$CdCl_2$	4.04	49.3	2511	110.0
$CdBr_2$	3.87	61.3	2493	101.7
CdI_2	3.01	82.1	2461	102.1
$PbCl_2$	4.81	53.8	2253	111.5
$PbBr_2$	4.03	62.5	2229	112.1
Na_3AlF_6	3.08	87.1		396.2
$BiCl_3$	0.47?	76.0	4707	
$LaCl_3$	3.88	73.8	4305	125.5
$PrCl_3$	4.85	72.3	4357	133.9
$NdCl_3$	3.92	69.6	4381	146.4