LAW OF CORRESPONDING STATE FOR THE TRANSPORT PROPERTIES OF MOLTEN SALTS

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Abstract

A theory of corresponding states is developed for the transport properties of strictly ionic fused salts. Using a model ionic melt introduced by Reiss, Mayer and Katz laws of corresponding states are obtained by dimensional analysis of the autocorrelation function expressions for the transport coefficients. The theory parallels Helfand and Rice's treatment of simple non-ionic fluids. Agreement between experiment and theory for several alkali halides and alkali nitrates is encouraging.

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I. Introduction

On the basis of a simple model ionic melt, Reiss, Mayer and Katz have developed a law of corresponding states for fused salts. The theory is moderately successful when applied to alkali halides, the alkaline earth fluorides and the alkaline earth oxides. Moreover, on the basis of the same model, Reiss, Katz and Kleppa[2] have developed a conformal solution theory which accounts for the heats of mixing of alkali nitrates, several of the alkali halides[3], alkali-alkaline earth halides[4], and alkali-alkaline earth nitrate[5] mixtures.

Reiss, Mayer and Katz define the properties of their model ionic melt with the following assumptions:

(1) The role of the long-range Coulomb interaction is to create a locally ordered structure wherein, on the average, a negative ion is surrounded by positive ions and a positive ion by negative ions.

(2) Both because of local structure and of the repulsive Coulomb interaction between ions of like sign, only short-range interactions between unlike ions are of importance. Thus the pair potential between like ions may be taken as

$$u_{\alpha\beta}(r) = \frac{(z_\alpha e)^2}{\kappa r} \quad ; \quad r \geq 0 \quad , \tag{1-1}$$

where z_α is the valence of ion α, e the electronic charge, r the distance separation and κ a local dielectric constant.

(3) The pair potential between unlike ions is taken to be

$$u_{\alpha\beta}(r) = \infty \quad ; \quad r \leq \lambda$$

$$= \frac{z_\alpha z_\beta e^2}{\kappa r} \quad ; \quad r > \lambda \quad . \tag{1-2}$$

Thus it is assumed that the short-range repulsive interaction between unlike ions is of the rigid core type and that there are no short-range attractive interactions (such as polarization and London dispersion terms) except those many-body effects accountable for by an effective dielectric constant, κ . Although the precise nature of the anion-cation hard core cutoff parameter, λ , is not known, an obvious choice is the sum of ionic radii, $\lambda = r_+ + r_-$.

The important feature of the RMK model lies in the conjecture that, due to local electroneutrality, the properties of an ionic melt are characterized by a single length parameter, λ . Thus the ionic melt is viewed as a pseudo-one-component system rather than an ionic mixture. In further support of the validity of this idea, Stillinger's[6] and Mayer's[7] work may be cited. Stillinger supposes that the compressibility of the molten alkali halides can be described with the hard sphere compressibility formula for a one-component system of hard spheres of diameter λ . The hard sphere formula is furnished by the scaled particle theory of Reiss, Frisch and Lebowitz[8]. Taking experimental compressibilities and the hard sphere formula, Stillinger calculates the parameter λ for most of the alkali halides. The value obtained for λ for each salt agrees rather well with Pauling's ionic crystal radii (actually Stillinger's λ's agree even better with the gas ionic radii). Carrying Stillinger's model further, Mayer shows that the thermal expansivities, surface tensions and compressibilities can be successfully interrelated by the scaled particles formulas with a single length parameter.

The purpose of this article is to develop for transport properties a theory of corresponding states based on the RMK fused salt model. A corresponding states theory could prove quite useful for estimating molten salt transport properties since there are not many data on molten salts. Furthermore, in measure of its success, our theory may assist in the formulation of an a priori theory of transport in fused salts. Our

treatment parallels a corresponding states theory developed by Helfand and Rice[9] for systems whose interaction potential is of the form $u = \epsilon\, u(r/\lambda)$.

II. Theory

The transport coefficients can be expressed in terms of time integrals of appropriate autocorrelation functions. Such expressions have been derived by Kubo et al[10] by consideration of the regression of fluctuations, which are assumed to follow macroscopic laws, and by Mori, who assumes that a local equilibrium distribution will relax rapidly to the equilibrium state. Their formulas for the shear viscosity and the thermal conductivity are

$$\eta = V^{-1} \int_0^\infty dt \int_0^{1/kT} d\beta \; \mathrm{tr} \left\{ J_{xy}^{(v)} \; e^{+i(t + i\hbar\beta)H/\hbar} \; J_{xy}^{(v)} \right.$$

$$\left. \cdot \; e^{-i(t + i\hbar\beta)H/\hbar} \; e^{-H/kT} \right\} \Big/ \mathrm{tr} \left\{ e^{-H/kT} \right\} \qquad (2\text{-}1)$$

and

$$\varkappa_t = V^{-1}T^{-1} \int_0^\infty dt \int_0^{1/kT} d\beta \; \mathrm{tr} \left\{ J_x^{(t)} \; e^{i(t + i\hbar\beta)H/\hbar} J_s^{(t)} \right.$$

$$\left. \cdot \; e^{-i(t + i\hbar\beta)H/\hbar} \; e^{-H/kT} \right\} \Big/ \mathrm{tr} \left\{ e^{-H/kT} \right\}. \qquad (2\text{-}2)$$

The subscript "t" on $\varkappa_t$ is to distinguish the thermal conductivity symbol from the dielectric constant $\varkappa$. Here the notation $\mathrm{tr}\left\{ \quad \right\}$ denotes the trace of the quantity enclosed in the curly brackets. $\underline{\underline{J}}^{(v)}$ is the microscopic pressure tensor given by the formula

$$\underline{\underline{J}}^{(v)} = \sum_i (\underline{p}_i \underline{p}_i/m_i + \underline{r}_i \underline{F}_i) - PV\underline{\underline{1}} \qquad (2\text{-}3)$$

with m_i , $\underline{p}_i$ and $\underline{r}_i$ the mass, momentum and position of particle i , and $\underline{F}_i$ the force on particle i ; t is the time, P the hydrostatic pressure and V the volume. The microscopic heat vector is

$$\underline{J}(t) = \sum_i \frac{p_i^2}{2m_i} \frac{\underline{p}_i}{m_i} + \frac{1}{2} \sum_i \sum_{i=j} (u_{ij}1 + \underline{r}_{ij}\underline{F}_{ij})\frac{\underline{p}_i}{m_i}$$

$$- \sum_i h_o^{(i)} \underline{p}_i/m_i \quad . \tag{2-4}$$

Here $h_o^{(i)}$ is the enthalpy of particle i , h Planck's constant and H the Hamiltonian whose classical form is

$$H = \sum_i [p_i^2/2m_i + \sum_j u_{ij}] \quad . \tag{2-5}$$

Helfand and Rice have shown that Eq. (2-1) and (2-2) lead to a corresponding states law for transport in the case of molecules whose pair potentials are of the form used by Pitzer, i.e. $u = \epsilon\, u(r/\lambda)$. Ours shall differ from their analysis only in that we use the RMK potential model.

To proceed let us consider symmetric salts and assume that the RMK potential model (defined by Eqs. (1-1) and (1-2)) suffices to represent the interactions between the ions composing the salts. At first we shall assume that in a particular salt the mass of the cation is equal to that of the anion, i.e. $m_A = m_C = m$; later we shall try to relax this requirement making use of the conjecture that unlike ion interactions are more important than like ion interactions. Now we are ready to dimensionally analyze Eqs. (2-1) and (2-2). Let us define the following reduced variables:

distance $\qquad\qquad r^* = r/\lambda \qquad\qquad\qquad$ (2-6)

pair potential $\qquad\qquad u^* = \frac{\varkappa\lambda}{z^2} u \qquad\qquad\qquad$ (2-7)

temperature $\qquad T* = \dfrac{\varkappa\lambda}{z^2} kT$ $\qquad\qquad\qquad$ (2-8)

pressure $\qquad P* = \dfrac{\varkappa\lambda^4}{z^2} P$ $\qquad\qquad\qquad$ (2-9)

volume $\qquad V* = V/\lambda^3$. $\qquad\qquad\qquad$ (2-10)

Through Newton's second law and the above reduced length and pair potential we obtain the additional reduced quantities

time $\qquad t* = \dfrac{(z^2/\varkappa\lambda)^{\frac{1}{2}}}{m^{1/2}\lambda}\, t$ $\qquad\qquad\qquad$ (2-11)

momentum $\qquad \underset{\sim}{p}* = \dfrac{1}{m^{1/2}(z^2/\varkappa\lambda)^{1/2}}\, p$ $\qquad\qquad\qquad$ (2-12)

Planck's Constant $\qquad \hbar* = \hbar / \lambda m^{\frac{1}{2}}(z^2/\varkappa\lambda)^{\frac{1}{2}}$ $\qquad\qquad\qquad$ (2-13)

With the above relations the Hamiltonian and the pressure tensor (and of course the heat vector) may be written in reduced form.

$$H* = \frac{\varkappa\lambda}{z^2} H = \Sigma_i [\frac{p_i^{*2}}{2} + \Sigma_j u*(r_{ij}^*)]$$ $\qquad\qquad\qquad$ (2-14)

$$\underset{\bar{\bar{}}}{J}^{(v)*} = \frac{\varkappa\lambda}{z^2} \underset{\bar{\bar{}}}{J}^{(v)} = \Sigma_i(\underset{\sim}{p}_i^*\underset{\sim}{p}_i^* + \underset{\sim}{r}_i\underset{\sim}{F}_i) - P*V*\underset{\bar{\bar{}}}{1} .$$ $\qquad\qquad\qquad$ (2-15)

The use of Eqs. (2-6) – (2-15) in Eq. (2-1) leads to the reduction

$$\eta* = \eta\,\lambda^2/m^{\frac{1}{2}}\,(z^2/\varkappa\lambda)^{\frac{1}{2}} = \frac{\lambda^{\frac{5}{2}}\varkappa^{\frac{1}{2}}}{m^{1/2}z}\, \eta$$ $\qquad\qquad\qquad$ (2-16)

where $\eta*$ is given by Eq. (2-1) with all the variables replaced by corresponding reduced variables. Thus $\eta*$ is a universal function of the reduced temperature,

pressure (or volume as $V* = V*(T*, P*, \hbar*))$ and Planck's constant; i.e.

$$\eta* = \eta*(T*, P*, \hbar*) . \qquad (2\text{-}17)$$

Since we are interested only in classical systems $(\hbar* = 0)$ we shall ignore $\hbar*$ in the argument of $\eta*$, i.e. we take

$$\eta* = \eta*(T*, P*) \qquad (2\text{-}18)$$

The thermal conductivity can be analyzed similarly to the above procedure for viscosity. The resulting universal function is

$$\kappa_t^*(T*, P*) = \frac{m^{\frac{1}{2}} \kappa^{\frac{1}{2}} \lambda^{\frac{5}{2}}}{kz} \kappa_t \qquad (2\text{-}19)$$

where we have already dropped $\hbar*$ from the argument of κ_t^* .

In their above form $\eta*$ and κ_t^* enjoy only limited usefullness because of the requirement that the anion and cation masses be equal (several salts for which this is roughly correct are NaF, KCl, RbBr, CaI, TlCl and MgO). In order to extend the utility of Eqs. (2-18) - (2-19), we conjecture that the dominant interactions giving rise to energy and momentum transport are the nearest neighbor, i.e. anion-cation interactions. That this is perhaps reasonable may be inferred from the success of the Stillinger-Mayer calculations, where it is seen that the anion-cation core inter- actions are dominant in determining the compressibility and thermal expansivity of simple fused salts. Their results emphasize the major importance of the short range anion- cation repulsive interactions in these dense liquids. This type of interaction is very efficient in collisional transfer of energy and momentum in dense systems where the movement of a particle is more or less restricted to a cage formed by its nearest neighbor molecules. In any case, if our conjecture is true, the only mass characterizing dynamical processes in molten salts will be, μ , the anion-cation reduced mass defined by

$$\mu = \frac{m_A m_C}{m_A + m_C} \qquad (2\text{-}20)$$

Thus, we shall scale the reduced quantities η^* and $\varkappa_t^*$ according to this reduced mass instead of m so that Eqs. (2-16) and (2-19) become

$$\eta^* = \frac{\lambda^{5/2} \varkappa^{1/2}}{(2\mu)^{1/2} z} \eta \qquad (2\text{-}21)$$

$$\varkappa_t^* = \frac{(2\mu)^{\frac{1}{2}} \varkappa^{\frac{1}{2}} \lambda^{\frac{5}{2}}}{kz} \varkappa_t \qquad (2\text{-}22)$$

m has been replaced by the quantity 2μ which reduces to m when the cation mass equals that of the anion.

Taking Eq. (2-21) - (2-22) for the reduced transport quantities is equivalent to assuming that a molten salt can be represented by a hypothetical molten salt composed of ions with identical masses, 2μ, but whose anions and cations have respectively the same radii as the anions and cations of the salt represented. As is the case with Stillinger's model, our model is expected to fail when the ratio of the anion to cation radius deviates greatly from unity, for then the probability of like-ion short-range encounters would be possible. The validity of our model is increased if the collisional contribution (represented by $r_i F_i$ in $J^{(v)}$) to transport is much greater than the kinetic contribution (the term $v_i p_i$ in $J^{(v)}$). The latter quantity represents the energy or momentum actually carried through fluid by a diffusing molecule. Obviously for this contribution the characteristic mass will be the mass of the diffusing molecule. At densities characteristic of molten salts the kinetic contribution is probably negligible. It has been theoretically estimated by Zwanzig[12] to be less than 1% for liquid argon. Using measured diffusion coefficients and a lattice model theory, Turnbull[13] has estimated the kinetic contribution to be no more than $3-4\%$ for molten $NaNO_3$ and $NaCl$.

Since the value of λ is somewhat uncertain, it is convenient to eliminate this quantity in Eqs. (2-21) - (2-22). This can be done following Reiss, Mayer and Katz's observation: the reduced pressure $P^*(T^*, V^*)$ is a universal function of T^* and V^* so that P^*_m, T^*_m and V^*_m, corresponding to the pressure, temperature and volume at the melting point, are universal constants. Now λ can be eliminated from the reduced quantities upon appropriate multiplication by the universal constant T^*_m. In particular, the quantities

$$\eta^*(\tau^*, \pi^*) = \frac{\sqrt{2}\,\eta^*}{(T^*_m/k)^{5/2}} = \frac{z^4}{\varkappa^2(\mu)^{1/2}T_m^{5/2}}\,\eta \tag{2-23}$$

and

$$\varkappa^*_t(\tau^*, \pi^*) = \frac{\varkappa^*_t}{\sqrt{2}\,(T^*_m/k)^{5/2}} = \frac{z^4(\mu)^{\frac{1}{2}}}{\varkappa^2 k\, T_m^{5/2}}\,\varkappa_t \tag{2-24}$$

are universal functions which may be considered as functions of $\tau^* = T/T_m$ and $\pi^* = P^*/T_m^{*4}$. These formulas are useful since to use them we need know only the thermodynamic quantity T_m.

Although the preceding analysis has been for symmetric salts, the generalization to unsymmetric salts is accomplished by defining the reduced temperature as

$$T^* = \varkappa\lambda T$$

leaving out the valence. Then, if z_A and z_C are the valence of the anion and cation respectively, it is straightforward to show that

$$\eta^* = \eta^*(T^*, P^*, z_A, z_C) = \frac{\lambda^{\frac{5}{2}}\varkappa^{\frac{1}{2}}}{(2\mu)^{1/2}}\,\eta \tag{2-25}$$

$$\varkappa^*_t = \varkappa^*_t(T^*, P^*, z_A, z_C) = \frac{(2\mu)^{\frac{1}{2}}\varkappa^{\frac{1}{2}}\lambda^{\frac{5}{2}}}{k}\,\varkappa_t \tag{2-26}$$

Thus salts having the same z_A and z_C will have corresponding properties according to Eqs. (2-25) - (2-26).

III. Comparison with Experiment

We have been unable to find thermal conductivity data on pure molten salts other than alkali nitrates; and viscosity data are rather sparse. However, the viscosity of several alkali halides has been measured as a function of temperature in the region of vapor-liquid coexistence. In this region the corresponding viscosity η'' is a function only of τ'' since the pressure is a function only of temperature. Thus in the coexistence region there should be a curve of η'' versus τ'' which is common to all conforming salts.

In Table 1 we have computed η'' for several alkali halides as a function of τ''. Observed viscosities and melting temperatures are used in the computation. Following Reiss et al we have assumed κ to be unity or at least constant for certain classes of salts. Reiss et al found that values of T_m^* computed, under the assumption that $\kappa = 1$, from Pauling's ionic radii and observed melting points were fairly constant for all the alkali halides except the lithium salts. From the entries in Table 1 we see that the salts NaCl, NaBr, KCl and KBr obey one corresponding state curve and NaI and KI obey another.

The values given for η'' in Table 1 are plotted versus τ'' in Figure 1. The data corresponding to NaCl, NaBr, KCl and KBr viscosities conform fairly well to the dashed curve described by the relation

$$\eta'' = 0.7512 \exp (4.6549/\tau'') \ . \tag{3-1}$$

This expression for η'' was obtained by a least squares fit of the data to the form

$\eta'' = B \exp(A/\tau'')$. The data on NaI and KI may be represented by the following least squares curve:

$$\eta'' = 2.164 \exp(4.0000/\tau'') \quad . \tag{3-2}$$

In the third column of Table 1 are entered values of η'' computed from Eq. (3-1) or Eq. (3-2), as the case may be. Of the twenty-one values listed, only three deviate by more than 10% from the experimental values. The fact that the data on the alkali iodides fall on a different curve from that of the other two halides is possibly due to variations in κ. However, at the moment we have no way of confirming this possibility. We are tempted to conclude that Eq. (3-1) would be useful in predicting viscosities for the cesium and rubidium chlorides and bromides while Eq. (3-2) could similarly be employed for cesium and rubidium iodides. The lithium halides have not been considered since even the RMK equilibrium corresponding states theory fails for these salts. The failure of the model for these salts is presumably due to complex ion formation, e.g. $LiCl_2^-$, in the liquid state.

Consider next thermal conductivity. Although we would expect the model to be more applicable to salts composed of structureless ions, we test it in Table 2 for the alkali nitrates. This is because we have no data on simple systems such as alkali halides. In the second column reduced thermal conductivities are given at various reduced temperatures. For lithium, sodium and potassium nitrate κ_t'' agrees quite well at corresponding temperatures. Silver nitrate is out of line. In the fourth column of Table 2, we have entered thermal conductivities computed from reduced thermal conductivities of potassium nitrate at the appropriate corresponding temperatures. The consistency among the alkali nitrate reduced thermal conductivities is remarkable considering the simplicity of the model. It should be recalled, however, that Reiss, Katz and Kleppa's successful conformal solution theory of the heats of

mixing of alkali nitrates was based on the simple hard-core-plus coulomb potential model.

The theory developed here seems promising on the basis of the experimental data considered. Hopefully, more data will be available in the near future and the theory can be subject to a more complete test.

Acknowledgements

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Table 1. Comparison of experimentally determined η^* with its least squares fit given by equations (3-1) and (3-2). Data taken from Molten Salt Chemistry, ed. M. Blander, Interscience, New York, 1964.

Compound	τ^*	$\dfrac{\eta_{exp}}{(\mu\ Tm^5)^{1/2}} = \eta^*$ $(gm^{1/2}/cm\text{-}sec\text{-}{}^{\circ}K^{5/2})$	Equation (3-1) or (3-2) $(gm^{1/2}/cm\text{-}sec\text{-}{}^{\circ}K^{5/2})$
NaCl	1.000	87.1	78.6
	1.045	70.2	65.0
	1.093	55.9	53.2
	1.140	44.9	44.5
	1.185	38.5	37.8
NaBr	1.050	68.3	63.0
	1.099	61.1	51.6
KCl	1.029	57.4	69.0
	1.123	45.2	47.2
KBr	1.010	68.6	74.7
	1.060	56.9	60.6
	1.104	50.8	50.5
KI	1.070	95.8	91.3
	1.121	76.0	76.9
	1.173	61.5	65.6
	1.223	50.4	57.0
NaI	1.042	95.7	99.9
	1.098	85.4	82.5
	1.150	72.8	70.4
	1.205	62.9	60.0
	1.260	55.0	51.6

Table 2. Calculation of κ_t^* and comparison of predicted κ_t (via KNO_3 data) with experimental κ_t.

Compound	τ^*	$\left(\dfrac{\mu}{Tm^5}\right)^{\frac{1}{2}}\dfrac{\kappa_t}{k} = \kappa_t^*$ $(10^3\ gm^{\frac{1}{2}}/cm\text{-}sec\text{-}{}^oK^{\frac{5}{2}})$	κ_t (experimental) $(10^{-4}\ cal/cm\text{-}sec\text{-}{}^oK)$	Predicted κ_t $(10^{-4}\ cal/cm\text{-}sec\ {}^oK)$
$LiNO_3$	1.054	24.4	15.7[a]	15.35
$NaNO_3$	1.040	26.4	13.2[b]	11.80
KNO_3	1.000	21.3	10.3[b]	---
	1.040	23.6	11.4[b]	---
	1.054	23.8	11.5[b]	---
A $AgNO_3$	1.000	42.4	9.0[b]	4.52
	1.040	47.1	10.0[b]	5.01

[a] L. R. White and H. T. Davis, private communication.

[b] Molten Salt Chemistry, ed. M. Blander, Interscience, New York, 1964.

Figure Caption:

Figure 1. Plot of experimental η'' versus τ'' for sodium and potassium chlorides,

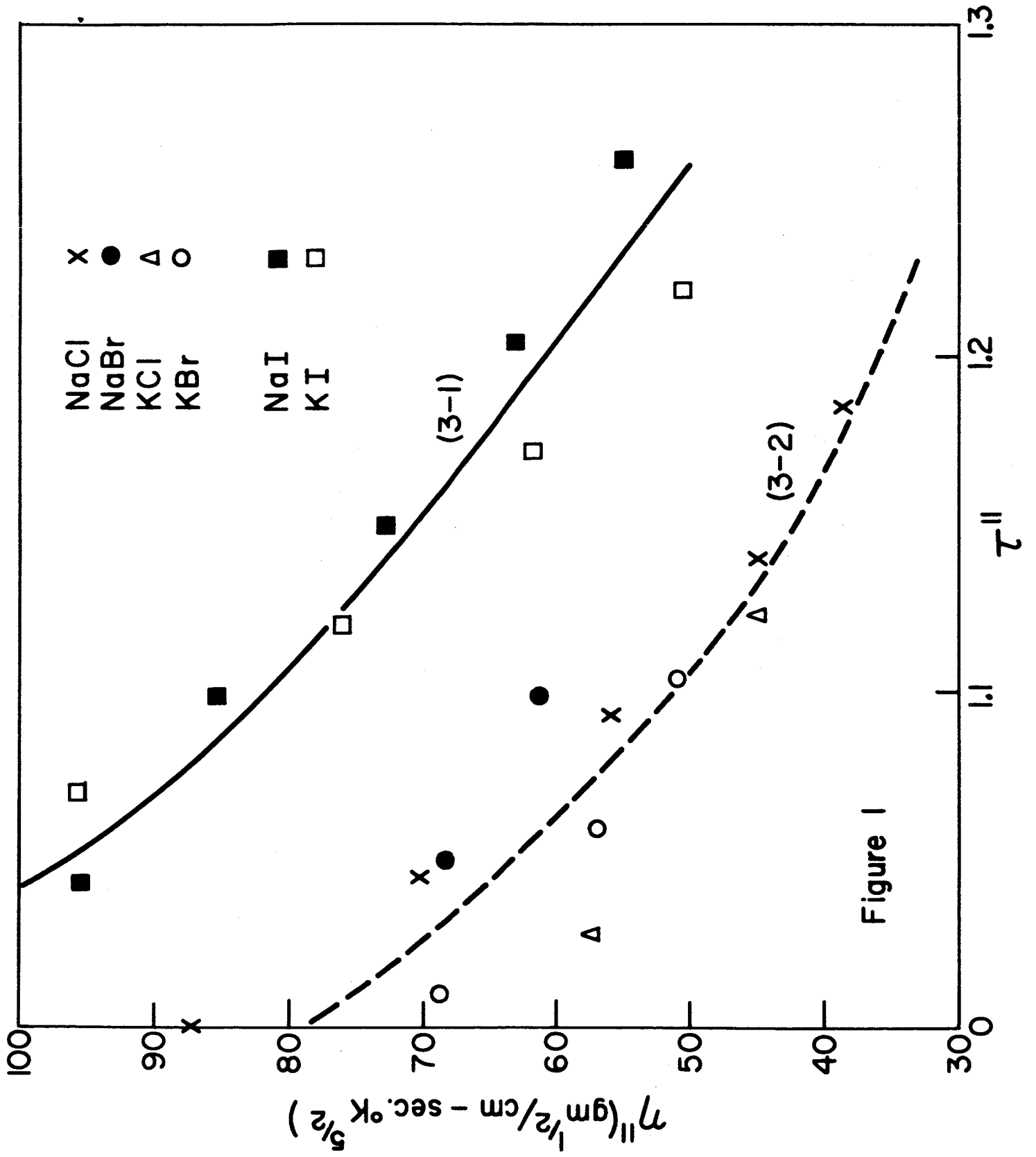bromides and iodides, with a comparison to the least squares fits of

(3-1) and (3-2).

Figure I