The Electrical Conductance of Molten Lead Chloride and Its Mixtures with Potassium Chloride

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The specific conductances of molten $PbCl_2$ + KCl mixtures have been measured as functions of temperature and composition, for the ranges *ca.* 500–800° and *ca.* 20–100 mol % $PbCl_2$, respectively. In the experimental temperature range the specific conductances of all melts follow (a) quadratic temperature dependences and (b) modified Arrhenius temperature dependences which can be expressed by equations due to Cohen and Turnbull and Adam and Gibbs. Bases for the interpretation of the composition dependence of conductance for these mixtures are examined, and the composition dependence is put on a rational basis in terms of the temperature T_0, a parameter associated with the temperature of zero free volume, or zero configurational entropy.

Introduction

The composition and (to a lesser extent) temperature dependences of the transport properties of binary salt mixtures have been the subject of many papers in the molten salt field. Deviations from additivity relationships of, *inter alia*, conductance isotherms have been used diagnostically to infer the constitutions of many mixtures. Such deviations have led, for example, to the hypothesis that complex anionic species exist in molten lead halide–alkali metal halide and cadmium halide–alkali metal halide mixtures.[1b] However, published interpretations of isotherms of conductance and other transport properties are open to doubt on several grounds. In particular, the absence of a suitable reference temperature for comparison of conductances makes deductions based on such comparison hazardous. It is not physically meaningful to ascribe differences in conductance of mixtures wholly to differences in the constitution of the mixtures, since the conductances may also differ because the comparison is made at nonequivalent temperatures.

It has been suggested that the freezing point be used as such a reference temperature,[1b,2] and that conductances be compared at temperatures θ_f given by

$$\theta_f = \alpha T_f \qquad (1)$$

where T_f is the liquidus temperature of a given mixture and α is a constant assigned arbitrary values (*e.g.*, 1.1, 1.2,...) However, the liquidus temperature of a given liquid mixture is determined at least as much by the structure of the solid phase formed on freezing as by the constitution to the liquid, so that T_f has no particular significance in respect to the transport properties of liquid mixtures. The critical temperatures would, perhaps, serve as reference temperatures, but again these are not governed wholly by the properties to the liquid phases and hence are still not entirely satisfactory.

The development of liquid free volume and other theories of transport processes in liquids now indirectly provides a sound basis for comparison of the transport properties of mixtures of different composition.[3-10]

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(1) (a) Department of Chemistry, Purdue University, West Lafayette, Ind. 47907; (b) H. Bloom and E. Heymann, *Proc. Roy. Soc.*, **A188**, 392 (1947).

(2) I. S. Yaffe and E. R. Van Artsdalen, *J. Phys. Chem.*, **60**, 1125 (1956).

(3) C. A. Angell, *ibid.*, **68**, 218, 1917 (1964); **69**, 2137 (1965); **70**, 2793 (1966).

(4) R. Araujo, *J. Chem. Phys.*, **44**, 1299 (1966).

(5) M. H. Cohen and D. Turnbull, *ibid.*, **31**, 1164 (1959).

(6) M. H. Cohen and D. Turnbull, *ibid.*, **34**, 120 (1961).

(7) G. Adam and J. H. Gibbs, *ibid.*, **43**, 139 (1965).

(8) H. Bloom and A. J. Easteal, *Aust. J. Chem.*, **19**, 1577, 1779 (1966).

(9) M. F. Lantratov and O. F. Moiseeva, *Russ. J. Phys. Chem.*, **34**, 367 (1960).

(10) C. T. Moynihan, *J. Chem. Educ.*, **44**, 531 (1967); *J. Phys. Chem.*, **70**, 3399 (1966).

Equation 2 has been found by Angell,[3] Araujo,[4] and other workers to describe well the temperature dependence of transport properties of several molten salts.

$$D,\ \Lambda T,\ \phi T = AT^{1/2}\exp[-k/(T - T_0)] \qquad (2)$$

θ = fluidity, D = diffusion coefficient, Λ = equivalent conductance, A, k, T_0 are constants. This equation is important because (a) it has a theoretical basis in the free volume theory of Cohen and Turnbull[5,6] and (b) the parameter T_0 can be regarded as a "built in" reference temperature on which comparison of transport properties of mixtures and pure salts can be rationally based.

In this study we have investigated in some detail (with respect to both temperature and composition) the electrical conductance of lead chloride + potassium chloride mixtures. This system was chosen because the investigation forms part of a broader study of lead halide based binary systems, of which the results of some emf studies have been published,[8] and because published data on the conductance of these mixtures[1b,9] have shown areas of marked disagreement and some curious features worthy of reinvestigation. Furthermore, lead chloride + potassium chloride mixtures have been studied by a variety of equilibrium and nonequilibrium techniques, so that many independent experimental data are available for use in testing models of these mixtures.

To determine the temperature dependence of conductance we have used a well established technique (see Experimental Section) to measure the specific conductances of the melts at small temperature intervals (*ca.* 5°).

The data can be fitted with high precision to four analytical functions, eq 2–5

$$\kappa = A'T^{-1/2}\exp[-k'/(T - T_0')] \qquad (3)$$

$$\kappa = A''\exp[-k''/T\ln(T/T_0'')] \qquad (4)$$

$$\kappa = a + bt + ct^2 \qquad (5)$$

where

$$t = {}^\circ\mathrm{C};\quad T = {}^\circ\mathrm{K};\quad \kappa = \text{specific conductance}$$

Of these, eq 3 is a simplified form of eq 2, and eq 4 is similar to an equation derived by Adam and Gibbs;[7] the parameter T_0 is the reference temperature referred to above. Equation 5 is a concise form in which to present the data and has implications to be discussed later; eq 2 has been used by Angell[3] and Moynihan[10] in analyses of the transport properties of other fused salts.

The composition dependence of specific conductance has been established from the measured conductances of pure $PbCl_2$ and of mixtures in the composition range 20–95 mol % $PbCl_2$ at intervals of *ca.* 5 mol %. This has been considered from both specific conductance isotherms and from graphs using θ_0 (eq 6) as a reference parameter

$$\theta_0 = \beta T_0 \qquad (6)$$

Experimental Section

Lead chloride was prepared from May and Baker Ltd. AnalaR lead nitrate and hydrochloric acid and was purified by crystallization from very dilute aqueous hydrochloric acid followed by filtration in the molten state, under a nitrogen atmosphere, through a (nominal) porosity 2 silica frit. Potassium chloride was purified by precipitation from a cold saturated solution of the AnalaR salt with dried hydrogen chloride. Mixtures were prepared by fusion of the appropriate quantities of the two salts under a nitrogen atmosphere. Each experiment required approximately 12 g of mixture for conductance measurements and analysis. Each mixture was analyzed for lead before and after an experiment, by conversion of samples to the nitrates and titration with aqueous sodium molybdate using 0.2% aqueous Solochrome Red B as an adsorption indicator. The sodium molybdate solution was standardized against lead nitrate prepared from 99.999% zone refined lead metal.

Apparatus

A conventional vertical tube furnace was used, with 19 swg Kanthal Al resistance wire wound on a silica support tube. The heating element was differentially wound to give a uniform temperature zone at the center of the furnace. The silica support tube (3.8 cm inside diameter) was closed at the base. The furnace was supplied with power *via* a Variac autotransformer.

Temperatures were measured with a calibrated platinum *vs.* platinum + 13% rhodium thermocouple and a Leeds and Northrup millivolt potentiometer (Model 8686). The thermocouple was guarded with a quartz tube attached to the conductance cell, and the hot junction of the thermocouple was approximately 5 mm distant from the melt in the cell capillary.

Conductances were measured with a conventional ac Wheatstone bridge constructed in our laboratories. The bridge was fed by a 1000-Hz fixed-frequency oscillator, with variable capacitors in parallel with a calibrated (accuracy ± 0.01%) Tinsley Type 2641 H.F.I. noninductive resistance box. The bridge was also fitted with calibrated ratio arms, of Sullivan noninductive resistors, to extend the resistance range by by factor of 10 for cell constant determinations.

The sensitivity of the bridge for conductance measurements was 0.05%; for cell constant determinations an extra high gain amplifier could be switched into the detection circuit resulting in a sensitivity of 0.05% for a 20,000-ohm resistance. All leads connecting the conductance cell, resistance box, and ratio arms to the bridge were coaxial. A Wagner earth was not used.

The conductance cell, which was of all-quartz construction, was essentially a U-shaped capillary with an attached thermocouple sheath, similar to that described by Yaffe and Van Artsdalen.[11] This design had the advantages that only small quantities of salt were required and that the cell constant was independent (within experimental precision) of the positions of the electrodes, provided they were completely immersed. The capillary was about 13 cm long with a bore of 0.7 ± 0.2 mm. Hollow cylindrical platinum electrodes were fabricated from 0.004-in. platinum sheet, and were welded to 26 swg platinum support wires. The electrodes were 2 cm long and 3 mm in diameter. To ensure a uniform temperature over the length of the capillary, the conductance cell was immersed in a bath of molten tin contained in a quartz tube which fitted closely into the furnace support tube. The surface of the tin was covered with charcoal to prevent excessive oxidation and subsequent attack (by oxides of tin) on the cell.

Experimental Procedure

Several cells were used in the course of the investigation; their cell constants were of the order 2500 cm^{-1}. The cell constant was determined with 1 demal solutions of potassium chloride in triple-distilled water at 25.00 ± 0.01°, using the value of specific conductance 0.11134 ohm cm^{-1} established by Jones and Bradshaw.[12] For each cell constant determination (made before and after each experiment) the electrodes were platinized according to the recommendations of Jones and Bollinger,[13] and before each measurement of melt resistance the electrodes were washed and heated to red heat until no flame coloration was observed.

Melt resistances were measured at temperature intervals of 3–4° while the melt cooled from approximately 760–800°, in most cases, to a lower limit determined by the liquidus temperatures of the mixtures (in the range 420–620°). In a typical experiment about 70 resistance measurements were made in the experimental temperature range. It was established that provided the cooling rate was not greater than about 3 deg min^{-1}, resistances determined during continuous cooling were within ±0.1% of the resistances measured at constant temperatures. After each experiment the cell and electrodes were cleaned with hot, concentrated aqueous solutions of ammonium acetate, washed with hot, distilled water, and soaked overnight in conductivity water. The cell was purged with nitrogen before each experiment.

Experimental Errors

A straightforward calculation shows that the cell constant at 1000° of a quartz cell of the type used in the present investigation is approximately 0.04% smaller than the value at 25°, and this temperature variation was neglected. The dimensional change in the platinum electrodes due to thermal expansion was also neglected, since the equivalent effect on cell resistance of variation in the position of the electrodes relative to the capillary was shown experimentally to be negligible (less than 0.03%). The accuracy of the cell constant determinations was ±0.1%, and on the average the cell constant changed by not more than 0.2% in the course of an experiment. The overall accuracy in specific conductances is considered to be within ±0.4%.

The compositions of the mixtures were determined to ±0.2 mol % $PbCl_2$. The average change in composition in the course of an experiment was 0.5 mol % $PbCl_2$, and the compositions quoted are considered to be accurate to ±0.4% $PbCl_2$.

Results

In addition to pure $PbCl_2$, mixtures of the following compositions were investigated (mol % $PbCl_2$): 93.6, 90.7, 83.7, 82.1, 79.6, 74.9, 70.3, 64.8, 59.3, 55.1, 49.0, 45.1, 41.4, 36.1, 29.8, 25.2, and 20.1.

The measured specific conductances of pure $PbCl_2$ obtained in this investigation are compared with published data in Table I. The close agreement indicates that the technique used for measuring conductance introduced negligible error into the data obtained.

Table I: Specific Conductance of $PbCl_2$

	Specific conductance		
T, °C	Present work[a]	Bloom and Heymann[1b]	Lantratov and Moiseeva[9]
500	1.450[b]	...	1.461
525	1.579[b]	...	1.570
550	1.701	...	1.696
560	1.750	1.75	...
575	1.820	...	1.819
600	1.932	1.92	1.931
625	2.038	...	2.040
650	2.139	2.13	2.13
700	2.323	2.34	...
720	2.389	2.39	...

[a] Frequency = 1000 Hz. [b] Extrapolated values from the analytical function for $PbCl_2$ (Table II).

The data for each mixture were fitted to a quadratic function of temperature, eq 5, using the IBM computer program POLRG, by the method of least-squares. This program allows a polynomial of degree seven or less to be fitted to the experimental data, and is formulated such that a calculation is terminated when the fit to the data is not improved by increasing the degree of the polynomial; in all cases the polynomial determined in this way was a quadratic. The parameters of these quadratics, together with the relative root-mean-square deviation of the experimental points from the computed curve, are given in Table II. It is important to note

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[11] I. S. Yaffe and E. R. Van Artsdalen, *J. Phys. Chem.*, **59**, 118 (1955).

[12] G. Jones and B. C. Bradshaw, *J. Amer. Chem. Soc.*, **55**, 1780 (1933).

[13] G. Jones and G. M. Bollinger, *ibid.*, **57**, 280 (1935).

Table II: Parameters for the Quadratic Temperature Dependence of Specific Conductance at 1000 Hz

$\kappa = a + bt + ct^2$ κ in $ohm^{-1}\ cm^{-1}$ t in °C

Composition, mol % $PbCl_2$	a	$b \times 10^3$	$c \times 10^6$	rms deviation, %	Exptl temp range, °C
20.1	−2.192	7.660	−3.056	2.33	650–940
25.2	−1.018	4.499	−0.972	0.31	620–790
36.1	−1.542	6.290	−2.549	0.19	530–750
41.4	−1.334	5.758	−2.215	0.12	470–760
45.1	−1.327	5.837	−2.280	0.19	470–780
49.0	−1.356	6.142	−2.571	0.27	450–780
55.1	−1.366	6.252	−2.598	0.17	450–750
59.3	−1.373	6.382	−2.626	0.20	450–750
64.8	−1.490	6.906	−2.965	0.14	440–750
70.3	−1.631	7.457	−3.335	0.15	430–790
74.9	−1.691	7.635	−3.307	0.14	430–780
79.6	−1.815	8.098	−3.568	0.24	420–780
82.1	−1.844	8.124	−3.506	0.47	440–770
83.7	−1.958	8.537	−3.815	0.36	450–780
90.7	−2.060	8.920	−3.968	0.31	460–800
93.6	−2.220	9.419	−4.226	0.16	480–770
100.0	−2.377	9.994	−4.687	0.23	540–770

that the conductances given by the parameters in Table II are for 1000 Hz, but deviations from the infinite frequency values are expected to be small.

For pure $PbCl_2$ and all the mixtures, graphs of log κ and log Λ *vs.* $1/T$ showed marked curvature. Equations 2, 3, and 4 fit almost all of the data well. Equivalent conductances were calculated from the measured specific conductances and the density data of Boardmann, Dorman, and Heymann.[14] The best-fit parameters of eq 2 are given in Table III. The fit of eq 2, 3, and 4 to the data for the 20.1 and 25.2 mol % $PbCl_2$ mixtures was poor, and the parameters for these mixtures have been omitted from Table III. Since the composition dependences of the parameters T_0' and T_0'' in eq 3 and 4 closely follow that of T_0 in eq 2, only the best-fit parameters for the latter equation are given.

Table III: Equivalent Conductance Parameters; $\Lambda = AT^{-1/2} \exp[-k/(T - T_0)]$

Composition, mol % $PbCl_2$	ln A	k(deg^{-1})	T_0, °K	rms deviation, %	Approximate uncertainty in T_0, °K
29.8	9.562	1507	196	0.16	±35
36.1	9.506	1453	218	0.15	±35
41.4	9.496	1518	192	0.13	±15
45.1	9.517	1569	175	0.13	±15
49.0	9.342	1368	209	0.16	±30
55.1	9.404	1449	189	0.13	±15
59.3	9.477	1513	172	0.16	±15
64.8	9.369	1340	209	0.12	±15
70.3	9.343	1289	222	0.11	±15
74.9	9.407	1329	218	0.13	±15
79.6	9.360	1248	238	0.18	±15
82.1	9.375	1262	238	0.18	±30
83.7	9.358	1237	244	0.14	±30
90.7	9.379	1247	242	0.14	±30
93.6	9.365	1194	260	0.11	±15
100	9.321	1138	272	0.10	±30

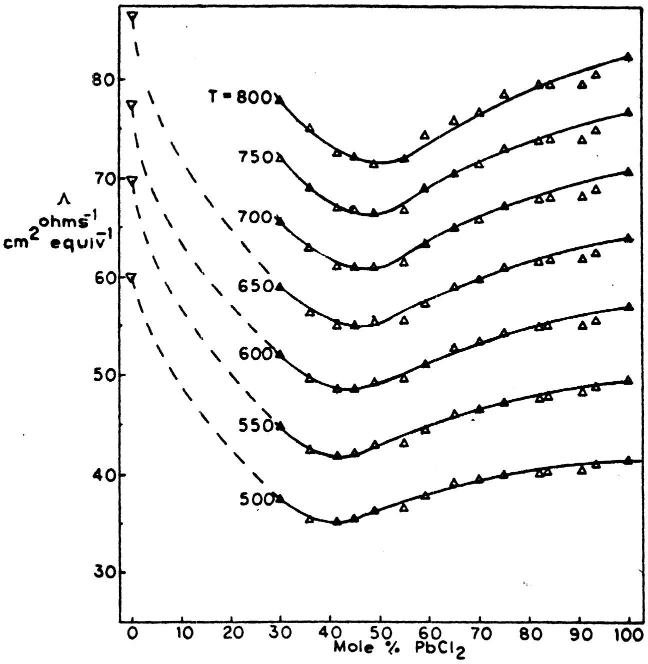

Figure 1. Equivalent conductance isotherms, T in °C: Δ, our data; ∇, from Yaffe and Van Artsdalen (ref 2).

Discussion Section

The results of this investigation, with regard to the isothermal composition dependence of equivalent conductance for the $PbCl_2$ + KCl system (Figure 1) agree

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[14] N. K. Boardmann, F. H. Dorman, and E. Heymann, *J. Phys. Colloid Chem.*, **53**, 375 (1949).

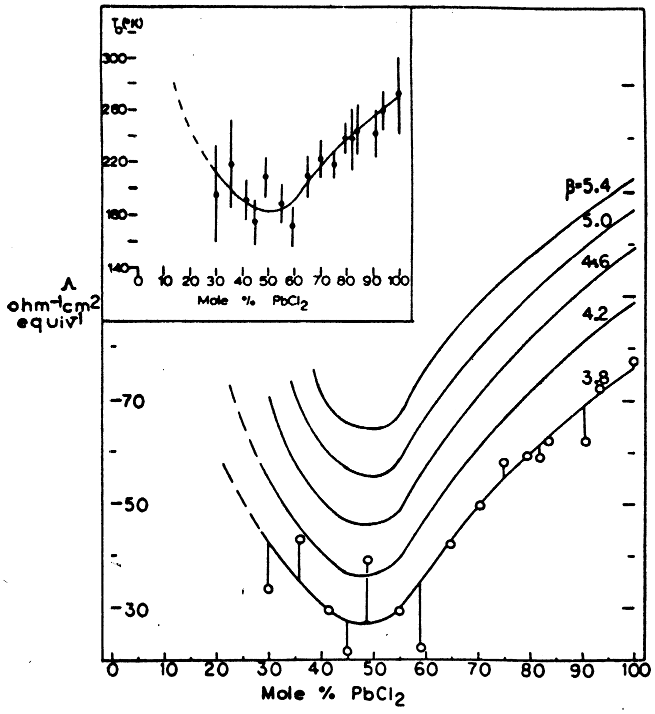

Figure 2. Equivalent conductance psuedo-isentropes, $\beta = T/T_0$. Inset, composition dependence of T_0.

well with those of Lantratov and Moiseeva.[9] The broad minimum at 40–50% $PbCl_2$ is common to both sets of data, and neither show the very small conductances at 20–25% $PbCl_2$ observed by Bloom and Heymann;[1b] the latter appears to be an erroneous feature of Bloom and Heymann's work.

Equation 5 has been found to describe the temperature dependence of specific conductance of molten alkali metal halides,[2] and of their binary mixtures,[11] and appears to be a general description of the temperature dependence of specific conductance.[15] A feature of this equation is that it predicts a maximum in conductance at a temperature given by

$$t = {}^{-b}/2c \tag{7}$$

Maxima in conductance *vs.* temperature graphs have been observed by Grantham and Yosim for several salts,[16] but our measurements did not extend to high enough temperatures to test this for the present system.

The magnitudes of the deviations from Arrhenius temperature dependence are illustrated by the large values of T_0 for eq 3. It follows that the transition state model of ionic migration is not valid for the $PbCl_2 + KCl$ system.

Equation 2 is based on the "free volume" model for transport properties due to Cohen and Turnbull,[5,6] in which T_0 is the temperature below which the free volume of the system is zero.

Equation 4 is based on the "co-operative rearrangement" model of Adam and Gibbs,[7] in which T_0'' represents the temperature below which the configurational entropy of the system is zero. The composition dependence of T_0'' is strikingly similar to the composition dependences of T_0 and T_0', suggesting that these parameters have a common origin. It can be shown mathematically that $T \ln (T/T_0'') = a + b\,(T - T_0'') = b(T - T_0')$, to within 1% over a 300° temperature range. Thus, apart from the preexponential function, equations 3 and 4 are functionally related.

The Cohen–Turnbull and Adam–Gibbs models are attempts to describe the glass transition phenomenon, and the parameters T_0 and T_0'' are the idealized temperatures at which the second-order transition responsible for the glass transition phenomenon occurs for infinitely slow cooling rates. The two models ascribe the glass transition to different causes, but it is evident that the parameters T_0 and T_0'' are both closely correlated with the experimental glass transition temperature T_g. This has been demonstrated experimentally for the system zinc chloride + pyridinium chloride,[17] and for other glass-forming systems.

The temperature T_g is clearly a function only of the liquid structure and is unaffected by properties of the vapor or of the crystalline solid. Glasses may be considered to be solids in which the liquid structure has been "frozen in," the chief characteristic which differentiates between glass and liquid being the mobility of the constituent entities. The temperature T_0 thus appears to be an ideal reference temperature for the liquid state.

In terms of the Adam–Gibbs model, T_0'' is related to the macroscopic thermodynamic parameters of the liquid by the equation

$$S_C = \Delta c_p \ln (T/T_0'') \tag{8}$$

where S_C = configurational entropy and Δc_p is the difference in heat capacities of the liquid and glassy states. If Δc_p is invariant with composition, then T/T_0'' is directly proportional to the configurational entropy of the liquid at temperature T. Thus comparisons of conductance at equal values of T/T_0'' may be considered to be made under isentropic conditions, and graphs of the composition dependence of conductance at equal values of T_0/T_0'' may be termed "isentropes." Because of the assumption made about Δc_p, and because T_0'' is only approximately the temperature of zero configurational entropy (see later discussion), we propose to call these graphs "pseudo-isentropes." The equivalent conductance pseudo-isentropes for the $KCl + PbCl_2$ system are given in Figure 2. The curves of Figure 2 have been plotted from equivalent conductances calculated from the best-fit parameters of eq 2.

(15) G. J. Janz, "Molten Salt Handbook," Academic Press, New York, N. Y., 1967, pp 290–297.

(16) L. F. Grantham and S. J. Yosim, *J. Phys. Chem.*, **67**, 2506 (1963); *J. Chem. Phys.*, **43**, 1415 (1965); **44**, 1509 (1966); **45**, 1192 (1966).

(17) A. J. Easteal and C. A. Angell, to be published.

The open circles show one set of calculated conductances. The scatter of the points about the curve is due in part to uncertainty in the density data from which the conductances were calculated; densities were available for only a few of the mixtures so that densities for most mixtures were obtained by interpolation of density isotherms. The inset of Figure 2 shows the composition variation of T_0, and it is the same (within the limits indicated) as the composition variations of T_0' and T_0''. The limits of uncertainty shown are the ranges of T_0 which correspond to ±1.5 times the minimum rms deviation of the experimental points from the curves calculated on the basis of eq 2. It can be seen that in the composition region rich in $PbCl_2$ the experimental scatter about the curve of best fit is quite small.

A comparison of the pseudo-isentropes with the isotherms of equivalent conductance indicates the usefulness of the concept of pseudo-isentropic comparison. Figure 2 shows a clearly defined minimum at 50 mol % $PbCl_2$, which does not shift with temperature (*i.e.*, with configurational entropy), whereas in Figure 1 the minimum is much broader and shifts from 40 mol % $PbCl_2$ at lower temperatures to 50 mol % $PbCl_2$ at higher temperatures. It is difficult to account for this shift in the isotherm minimum. On the other hand, the pseudo-isentropes indicate that the structural characteristics responsible for the decrease in conductance do not change with temperature. Furthermore, the composition at which the pseudo-isentrope minimum occurs corresponds to the stoichiometry of the entity $PbCl_3^-$, which has been postulated to account for, *inter alia*, vapor pressure data.[18] A tentative correlation of T_0'' (and T_0, T_0') with ion association in $PbCl_2 + KCl$ mixtures is thus suggested, but a more detailed interpretation is not justified on the basis of the results reported here.

Because the absolute magnitudes of T_0, T_0', and T_0'' are not significant it cannot be said that they are precisely the temperatures of zero free volume (and configurational entropy) and similarly the other parameters have no unambiguous interpretation. However, T_0, T_0', and T_0'' should be reasonably good approximations to these temperatures.

The closeness of fit of the functions defined by eq 3 and 4 to the experimental conductance data (rms deviation 0.1–0.2%) is suggestive that the mechanism of ionic transport in $PbCl_2 + KCl$ electrolytes is related to a cooperative rearrangement mechanism. However, the fact that quadratic functions of temperature (eq 5) fit the data almost equally well on the whole indicates that some caution must be exercised in applying a cooperative relaxation model to these liquids. Indeed there may be still further functional relationships between conductance and temperature which fit the data with precision of the same order as for the functions discussed here (the Arrhenius equation is a notable exception), and which are derivable from quite different transport mechanisms. A more decisive assessment of the applicability of cooperative relaxation and liquid free volume type models to these electrolytes must await detailed analyses of the temperature dependence of precise data for other transport properties of the mixtures and/or estimation of T_0 from heat capacity data.

Conclusions

The use of the temperatures of zero free volume or zero configurational entropy, as a reference temperature appears to be useful for $PbCl_2 + KCl$ fused mixtures. Similar analyses of transport data for other high-temperature molten electrolytes may well yield more detailed interpretations of such data than have been obtained previously.

Acknowledgment. We are indebted to C. A. Angell and C. T. Moynihan for helpful and stimulating discussions, and the New Zealand Universities Research Grants Committee for an equipment grant.

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[18] K. Hagemark, D. Hengstenburg, and M. Blander, *J. Phys. Chem.*, 71, 1819 (1967).