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First Dissociation Constant of *o*-Phthalic Acid and Standard pH Values for 0.05 *m* Potassium Hydrogen Phthalate in 50 wt % Ethanol/Water Solvent from 25 to −10 °C

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Recent IUPAC criteria regarding pH measurements in aqueous and aqueous–organic media suggest that 0.05 *m* potassium hydrogen phthalate (KHPh) be used as the reference buffer solution for pH standardization. In this context, values of the first ionization constant of *o*-phthalic acid in 50 wt % ethanol/water were determined by electromotive force measurements (emf) of cells of the type Pt(Pd);H_2(g, 1 atm)|H_2Ph(*m*), KHPh(*m*), NaCl(*m*) in 50 wt % C_2H_5OH/H_2O|AgCl;Ag over the temperature range 25 to −10 °C. Values of pK_1 were fitted to an equation of the form $pK = A/T + B + C \ln T$ (s = 0.0008 pK unit) which allowed evaluation of thermodynamic state functions ($\Delta G°$, $\Delta H°$, $\Delta S°$, and $\Delta C_p°$) for the dissociation process. Further measurements of cells Pt(Pd);H_2(g, 1 atm)|KHPh(*m*=0.05) + NaCl(*m*) in 50 wt % C_2H_5OH/H_2O|AgCl;Ag allowed the assignment of standard pH(RVS) for the 0.05 *m* phthalate buffer in the solvent mixture over the same temperature range.

Introduction

Recently approved IUPAC criteria for standardization of pH measurements in aqueous (*1*) and aqueous–organic media (*2*) designate 0.05 *m* potassium hydrogen phthalate (KHPh) as the reference value pH standard, pH(RVS). In view of the widespread application of certain nonaqueous and mixed solvents in chemical and biochemical research, standard methods for pH measurement and control in these media are needed.

In a recent contribution (*3*) we reported values of the standard potential of the silver–silver chloride electrode ($E°_m$) in 50 wt % ethanol/water solvent over the temperature range 25 to −10 °C; those results allow for further studies, by emf methods, of weak acid behavior in this solvent medium at these temperatures.

We have now determined the first dissociation constant (pK_1) of *o*-phthalic acid (H_2Ph) in 50 wt % ethanol/water by emf measurements of the cell

Pt(Pd);H_2(g, 1 atm)|H_2Ph(*m*), KHPh(*m*),
NaCl(*m*) in 50 wt % C_2H_5OH/H_2O|AgCl;Ag (A)

where the molality (*m*) was varied from 0.005 to 0.05 mol kg^{-1} and the temperature at 5-deg intervals over the range 25 to −10 °C. Supplemental measurements of cells of the type

Pt(Pd);H_2(g, 1 atm)|KHPh(*m*=0.05),
NaCl(*m*) in 50 wt % C_2H_5OH/H_2O|AgCl;Ag (B)

with m_{NaCl} varied from 0.01 to 0.06 mol kg^{-1} led to the assignment of conventional activity pH(RVS) values for the phthalate buffer in the mixed solvent over the same temperature range.

Table I. Standard Potential ($E°_m$) of the Ag;AgCl Electrode and Debye–Hückel Constants in 50 wt % Ethanol/Water[a] from 298.15 to 263.15 K

		Debye–Hückel const	
T, K	*E*°, V	*A*	*B*
298.15	0.185 50	0.9852	0.3968
293.15	0.189 77	0.9720	0.3956
288.15	0.193 86	0.9585	0.3943
283.15	0.197 73	0.9460	0.3931
278.15	0.201 38	0.9342	0.3920
273.15	0.204 78	0.9230	0.3910
268.15	0.207 95	0.9121	0.3899
263.15	0.210 98	0.9019	0.3890

[a] Mole fraction of ethanol in this mixture is 0.2180.

Experimental Section

Anhydrous absolute ethanol was obtained from U.S. Industrial Chemical Co. and used without further purification. Reagent grade *o*-phthalic acid (Sigma 99%) and potassium hydrogen phthalate (Sigma 99+%) were dried for at least 2 h at 110 °C before use. Reagent grade sodium chloride was recrystallized twice from 50% methanol/water and dried at 110 °C. Deionized water containing less than 0.4 ppm dissolved salts (as NaCl) was distilled once in an all-glass still.

The silver–silver chloride electrodes were prepared as described elsewhere (*4*) and stored in 0.01 *m* NaCl (in the mixed solvent) for at least 24 h before use. Bias potentials among the electrodes never exceeded 0.02 mV. Palladium electrodes for use in the hydrogen electrode compartments were prepared by electrolyzing 2-cm^2 platinum foils in a 1 M HCl solution approximately 0.1 M in palladous chloride; electrolysis was carried out for 5 min at 50 mA.

The cells were of all-glass construction equipped with a triple saturator for the entering hydrogen gas. Hydrogen was purified with a De-oxo (Engelhard) catalytic purifier. Temperature control to ±0.05 °C was maintained by immersion of the cells in an insulated bath equipped with a refrigerated circulating unit and a proportional temperature controller. The bath solution was 50% ethylene glycol/water.

All emf measurements were run in duplicate and the results averaged. Measurements were made initially at 25 °C. The cells were then allowed to attain −10 °C overnight, after which readings were taken at 5-deg intervals, returning to 25 °C. The cells displayed excellent stability, the initial and final values at 25 °C differing by no more than 0.06 mV on the average.

Results

The standard potentials used in the calculations were obtained from ref *3* and are reproduced in Table I, along with the Debye–Hückel constants *A* and *B* for the mixed solvent at each temperature. The emf data were corrected to 1 atm (101.325 kPa, 760 mmHg) partial pressure of hydrogen as described earlier (*3*).

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Table II. Corrected Emf Values for the Cell Pt(Pd);H_2(g, 1 atm)|H_2Ph(m), KHPh(m), NaCl(m) in 50 wt % C_2H_5OH/H_2O|AgCl;Ag from 25 to –10 °C

m	25 °C	20 °C	15 °C	10 °C	5 °C	0 °C	–5 °C	–10 °C
0.049 96	0.481 27	0.481 42	0.481 53	0.481 58	0.481 60	0.481 55	0.481 52	0.481 45
0.041 04	0.486 28	0.486 34	0.486 34	0.486 30	0.486 22	0.486 09	0.485 97	0.485 81
0.032 00	0.492 64	0.492 58	0.492 57	0.492 31	0.492 10	0.491 83	0.491 60	0.491 30
0.023 03	0.501 85	0.501 62	0.501 34	0.500 99	0.500 62	0.500 22	0.499 84	0.499 42
0.013 99	0.514 65	0.514 20	0.513 69	0.513 11	0.512 50	0.511 85	0.511 22	0.510 59
0.005 003	0.542 24	0.541 30	0.540 28	0.539 77	0.538 02	0.536 86	0.535 73	0.534 58

Table III. pK_1 of Phthalic Acid in 50 wt % Ethanol/Water from 298.15 to 263.15 K

T, K	pK_1	10^3s^a	T, K	pK_1	10^3s^a
298.15	3.685	3.9	278.15	3.762	3.7
293.15	3.700	3.8	273.15	3.792	3.8
288.15	3.717	3.8	268.15	3.828	3.7
283.15	3.738	3.7	263.15	3.868	3.8

[a] Standard deviation of the intercept.

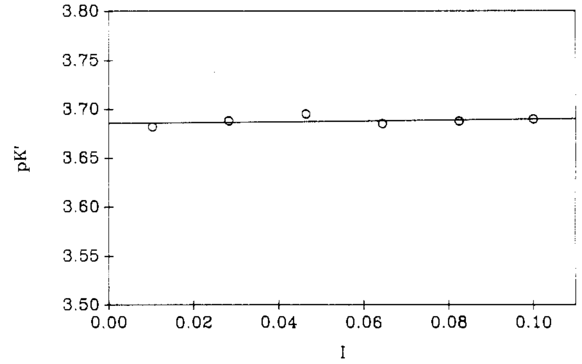

Figure 1. Plot of pK' vs I for phthalic acid in 50 wt % ethanol/water at 298.15 K.

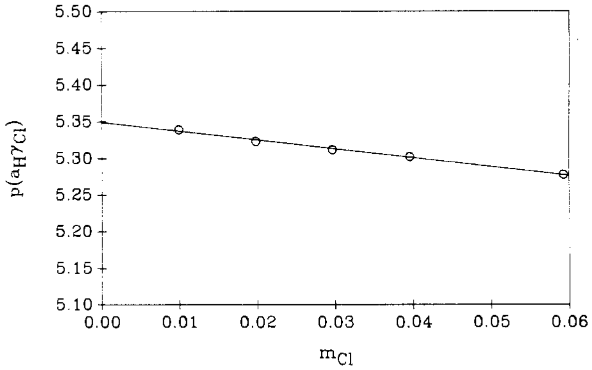

Figure 2. Plot of $p(a_H\gamma_{Cl})$ vs m_{Cl} from emf data on the cell Pt(Pd);H_2(g, 1 atm)|KHPh(m=0.05) + NaCl(m) in 50 wt % ethanol/water|AgCl;Ag at 298.15 K.

1. First Dissociation Constant (pK_1) of o-Phthalic Acid. The results of the emf measurements of cell A leading to the calculation of pK_1 for H_2Ph are given in Table II. Six cell solutions containing equal molalities of H_2Ph, KHPh, and NaCl spanning the range 0.05–0.005 m were tested. Values of pK_1 were obtained by linear extrapolation of the function pK' to I = 0

$$pK' = -\log\,[K_1(\gamma_{Cl}/\gamma_{HPh})] = (E - E^\circ)/k + \log\,[m(m - m_H)/(m + m_H)]$$

$$\equiv pK_1 - bI \qquad (1)$$

where I is the ionic strength and k is written for (RT ln 10)/F. Equation 1 is derived from the mass-action expression for the dissociation process, $H_2Ph \leftrightarrow H^+ + HPh^-$

$$K_1 = a_H m_{HPh}\gamma_{HPh}/m_{H_2Ph} \qquad (2)$$

combined with the Nernst equation for cell A. The activity coefficient of the uncharged acid (H_2Ph) is taken to be unity. The ionic strength, I, of the cell A solutions is given by $2m + m_H$; the contribution of phthalate ion (Ph^{2-}) is considered negligible. Initially I was taken as $2m$, from which m_H was estimated from the emf of cell A and the relations

$$-\log m_H = -\log\,(a_H\gamma_{Cl}) - \frac{2AI^{1/2}}{1 + 4.57BI^{1/2}}$$

$$= E - E^\circ + \log m_{Cl} - \frac{2AI^{1/2}}{1 + 4.57BI^{1/2}} \qquad (3)$$

where a Debye–Hückel expression is used to approximate the square of the mean activity coefficient of HCl (γ_{HCl}^2). The value å = 4.57 was chosen for consistency with the Bates–Guggenheim convention (*5*). Once m_H was estimated, a refined value of I was calculated and iterations continued until self-consistent values of I and m_H were obtained.

The ionic strength dependence of pK' is not expected to be large; it arises from specific ion–ion interactions which may cause the ratio γ_{Cl}/γ_{HPh} (eq 1) to depart from unity at high concentrations of electrolyte. Figure 1 is a plot of pK' vs I at 25 °C. Table III lists the pK_1 values calculated over the temperature range 25 to –10 °C, along with the standard deviation of the intercept, s.

2. Standard pH(RVS) Values. Table IV lists the emf values obtained from cell B containing 0.05 m KHPh with added NaCl(m). Five cell solutions with m_{NaCl} in incremental molalities over the range 0.01–0.06 mol kg^{-1} were measured. These data permitted calculation of the acidity function, p($a_H\gamma_{Cl}$), defined by

$$p(a_H\gamma_{Cl}) = (E - E^\circ)/k + \log m_{Cl} \qquad (4)$$

Extrapolation of this function to m_{Cl} = 0 yields on intercept,

Table IV. Corrected Emf Values for the Cell Pt(Pd);H_2(g, 1 atm)|0.05 m KHPh + NaCl(m) in 50 wt % C_2H_5OH/H_2O|AgCl;Ag from 25 to –10 °C

m	25 °C	20 °C	15 °C	10 °C	5 °C	0 °C	–5 °C	–10 °C
0.059 29	0.570 29	0.568 56	0.566 74	0.564 95	0.563 11	0.561 21	0.559 32	0.557 35
0.039 51	0.582 18	0.580 27	0.578 24	0.576 31	0.574 28	0.572 20	0.570 17	0.568 11
0.029 56	0.590 20	0.588 39	0.586 14	0.584 01	0.581 85	0.579 65	0.577 52	0.575 39
0.019 76	0.601 21	0.599 11	0.596 78	0.594 51	0.592 19	0.589 83	0.587 48	0.585 11
0.009 892	0.619 94	0.617 70	0.615 06	0.612 51	0.609 82	0.607 22	0.604 60	0.601 91

Table V. Conventional pH(RVS), $p(a_H\gamma_{Cl})°$, and Ionic Strength (I) Values for 0.05 m Potassium Hydrogen Phthalate in 50 wt % Ethanol/Water from 25 to -10 °C

t, °C	25	20	15	10	5	0	-5	-10
pH(RVS)[a]	5.191 (4.008)[b]	5.207 (4.000)	5.218 (3.997)	5.235 (3.996)	5.255 (3.999)	5.283 (4.005)	5.314	5.349
$p(a_H\gamma_{Cl})°$	5.349	5.363	5.372	5.388	5.406	5.431	5.461	5.494
10^3s[c]	1.9	2.4	2.3	2.8	2.5	2.9	3.0	2.6
10^2I	5.105	5.105	5.107	5.108	5.109	5.110	5.112	5.114

[a] pK_2 = 7.00. [b] pH(RVS) values in water are enclosed in parentheses. [c] Standard deviation of the intercept.

Table VI. Thermodynamic Functions for the Dissociation of Phthalic Acid in 50 wt % Ethanol/Water at 298.15 K

$\Delta G°$, kJ mol^{-1}	21.04
$\Delta S°$, J mol^{-1} K^{-1}	-56.99
$\Delta H°$, kJ mol^{-1}	4.045
$\Delta C_p°$, J mol^{-1} K^{-1}	-206.3

$p(a_H\gamma_{Cl})°$, from which the "conventional" pH(RVS) can be assigned:

$$\text{pH(RVS)} = -\log a_H = p(a_H\gamma_{Cl})° - AI^{1/2}/(1 + 4.57BI^{1/2}) \tag{5}$$

where the Debye-Hückel term is used to estimate log γ_{Cl}. Figure 2 is a typical plot of $p(a_H\gamma_{Cl})$ as a function of m_{Cl} at 25 °C. Table V lists the intercepts $p(a_H\gamma_{Cl})°$ and their standard deviations at the eight temperatures studied. Also included are the conventional pH(RVS) values and ionic strengths (I) for 0.05 m KHPh in 50 wt % ethanol/water over the entire temperature range.

Discussion

The pK data summarized in Table III are given by the equation

$$pK = 3423.0/T - 69.1715 + 10.7723 \ln T; \quad s = 0.0008 \tag{6}$$

where T is the thermodynamic temperature. Table VI lists the corresponding thermodynamic quantities at 298.15 K for the dissociation process. The $\Delta G°$ value obtained at 298.15 K in the mixed solvent (21.04 kJ/mol) is higher than that measured in water (16.84 kJ/mol), corresponding to a free energy of transfer of 4.202 kJ/mol. This is an indication of a destabilization of the dissociation process as alcohol is added to the aqueous medium. This effect is to be expected for the dissociation of uncharged acids and has been observed for phthalic acid in other aqueous-organic mixtures such as dioxane/water (*6*) and acetonitrile/water (*7*), as well as for acetic acid in ethanol/water (*8*).

The pH(RVS) values for 0.05 m KHPh summarized in Table V were calculated on the assumption that K_2 is at least 3 orders of magnitude smaller than K_1 over the temperature range studied. The rationale for this assumption and the method of pH(RVS) assignment follow.

The extrapolations of the plots $p(a_H\gamma_{Cl})$ vs m_{Cl} at the eight temeratures yield intercepts, $p(a_H/\gamma_{Cl})°$, which are 1.5 units higher than pK_1 on the average. As the pH of a solution of the primary salt of a diprotic acid should lie approximately halfway between pK_1 and pK_2, one expects that pK_2 should not fall below 6.5 over the range of pK_1 values determined here. Furthermore, we have found that the pH(RVS) value calculated is not very sensitive to choice of pK_2 when the latter is above 6.5, where 1.0 unit in pK_2 corresponds to a change of only 0.002 pH unit by our method of calculation. Table VII lists pH values for several choices of pK_2.

For assignment of pH(RVS) to the 0.05 m KHPh solution, we considered the following equilibria:

$$2\text{HPh}^- \leftrightarrow \text{H}_2\text{Ph} + \text{Ph}^{2-} \qquad K_2/K_1 \tag{7}$$

$$\begin{array}{ccccc} \text{HPh}^- & \leftrightarrow & \text{H}^+ & + \ \text{Ph}^{2-} & K_2 \\ (0.05 - 2x - m_H) & & m_H & (x + m_H) & \end{array} \tag{8}$$

where it is evident that the equilibrium denoted by eq 7 dominates. The symbol x represents the molality of H_2Ph. The ionic strength of the solution can be shown to be

$$I = (0.05 + x + 2m_H) \tag{9}$$

Hydrogen ion molality, m_H, was calculated from $p(a_H\gamma_{Cl})°$ using eq 3 and a reasonable estimate of I. Again, an iterative approach was taken with m_H calculated using I = 0.05 m as a first approximation. The term x was then determined by consideration of eq 8 and the relation (*9*)

$$K_2/K_1 = \frac{x(x + m_H)\gamma_\pm^2}{(0.05 - 2x - m_H)^2} \tag{10}$$

where the Debye-Hückel term was used to estimate the activity coefficient in a fashion analogous to eq 3 and 5. Ionic strength was recalculated from eq 9 and the process repeated until self-consistent values were obtained. Equation 5 yielded the sought-after pH(RVS).

It should be emphasized that, as a measure of acidity or free proton activity, direct comparison of pH(RVS) obtained in the mixed solvent with those in the purely aqueous medium (Table V) is not possible without knowledge of the "transfer" activity coefficient, $_m\gamma_H$, or the so-called "medium effect" for the proton, a term that is not measurable and, at present, is without an universally accepted convention for its calculation. The pH(RVS) values reported here, however, may prove useful for the calibration of pH meter assemblies in 50 wt % ethanol/water solvent and for obtaining accurate pH values for use in thermodynamic calculations in this solvent medium.

Table VII. Effect of pK_2 on Calculated pa_H for 0.05 m Potassium Hydrogen Phthalate in 50 wt % Ethanol/Water from 25 to -10 °C

	t, °C							
pK_2	25	20	15	10	5	0	-5	-10
6.0	5.188	5.204	5.215	5.233	5.252	5.279	5.310	5.345
6.5	5.189	5.205	5.216	5.234	5.254	5.281	5.312	5.347
7.0	5.191	5.207	5.218	5.235	5.255	5.283	5.314	5.349
7.5	5.191	5.207	5.218	5.236	5.256	5.283	5.314	5.349

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Literature Cited

(1) Covington, A. K.; Bates, R. G.; Durst, R. A. *Pure Appl. Chem.* **1983**, *55*, 1467.
(2) Mussini, T.; Covington, A. K.; Longhi, P.; Rondinini, S. *Pure Appl. Chem.* **1985**, *57*, 865.
(3) White, D. R.; Warner, P. *J. Chem. Eng. Data* **1988**, *33*, 174.
(4) Bates, R. G. *Determination of pH*, 2nd ed.; Wiley: New York, 1973; Chapter 10.
(5) Bates, R. G.; Guggenheim, E. A. *Pure Appl. Chem.* **1960**, *1*, 163.
(6) Mussini, T.; Cicognini, M.; Longhi, P.; Rondinini, S. *Anal. Chim. Acta* **1984**, *162*, 103.
(7) Mussini, T.; Longhi, P.; Rondinini, S.; Tettananti, M.; Covington, A. K. *Anal. Chem. Acta* **1985**, *174*, 331.
(8) Bates, R. G.; Bennetto, H. P.; Sankar, M. *Anal. Chem.* **1980**, *52*, 1598.
(9) Bates, R. G. *J. Am. Chem. Soc.* **1948**, *70*, 1579.

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Surface Tension and Electrical Conductivity of Molten Thiocyanates MSCN (M = Na, K, Rb, and Cs)

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Surface tensions and electrical conductivities of molten thiocyanates MSCN (M = Na, K, Rb, and Cs) have been measured by the maximum bubble pressure method and the ac bridge method, respectively, and their values were expressed as functions of temperature. Both results for MSCN melts were found to be close to those of typical ionic melts such as nitrates and halides.

Introduction

A linear SCN^- ion is present in alkali-metal thiocyanate melts near their melting points (*1–3*) as well as in the solid state (*4–8*). Physicochemical properties of the melts with such an ion are of interest in the comparison with those of alkali-metal halide and nitrate melts. Some properties for molten potassium and sodium thiocyanates have been reported by Ubbelohde et al. (*9*, *10*), Jindal and Harrington (*11*), and Cingolani et al. (*12*). However, there are little data reported on the other alkali-metal thiocyanate melts. In order to systematically study properties of the melts, we measured the densities and refractive indexes of a series of alkali-metal thiocyanate melts (*13*) and evaluated an electronic polarizability of SCN^- ion in the molten state using their results (*14*). In the present study, the surface tensions and electrical conductivities of MSCN (M = Na, K, Rb, and Cs) melts were measured following the previous work, in which molten LiSCN was excepted because of its thermoliability.

Experimental Section

Materials. Chemicals used for the present studies were >99.9% pure (Rare Metal Co., Ltd.) and were dried at the temperatures 30 K below their melting points (*6*, *9*, *10*) under a reduced pressure of 0.13 Pa for 8 h.

Surface Tension. For the measurements of the surface tension the maximum bubble pressure method was applied because of its precision at high temperatures. Argon was used as a working gas, and it was purified by passing though chemical traps filled with molecular sieves (4A) and titanium sponges at 1173 K to remove possible H_2O, N_2, and O_2 contaminations. Pressure fluctuations of the gas were buffered by two 5-dm^3 buffer tanks. The gas flow was adjusted with a needle valve. A fused-silica tube was attached to a micrometer screw. A capillary tube of Pt–10% Rh alloy (2-mm outer diameter, 0.2 mm thick, 80 mm long) sharpened to a knife edge at the tip was attached to the lower end of the silica tube with a graphite joint. A manometer filled with *n*-butyl phthalate colored red by a dyestuff and kept at 303.5 ± 0.1 K by thermostated water was used to measure the pressure of the working gas bubble. The temperature of the furnace was maintained within ±1 K with a controlling device, and the temperature of the melt was measured with a C.A. thermocouple sheathed with a fused-silica tube. A fused-silica crucible containing the sample was set in the furnace, and then the atmosphere in the furnace was exchanged with the working gas. A detailed procedure of the measurement was described elsewhere (*15*).

The inner diameter of the capillary tip was determined by a measurement of the surface tension of distilled water at room temperature, and its diameter at the elevated temperature was corrected by use of the coefficient of thermal expansion for the alloy (*16*).

According to Nissen and Carlsten (*17*), the surface tension, γ, of the melt is calculated from

$$\gamma = rg(hd_1 - id_2)/2 - d_2 r^2 g/3 - d_2^2 r^3[12hd_1 - id_2] \qquad (1)$$

where $2r$ is the inside diameter of the capillary, g the acceleration due to gravity, h the height of manometer, d_1 the density of *n*-butyl phthalate, which was measured pycnometrically, d_2 the density of the melt, and i the depth of immersion into the melt of the capillary.

Prior to the measurements of the melt samples, the surface tensions of molten $NaNO_3$ and KNO_3 were measured to obtain the precision of this apparatus, and comparisons were made among the recommended values (*18*, *19*) and observed ones. At 673 K, percent departures for $NaNO_3$ and KNO_3 were found to be 0.29% and 0.21%, respectively. Similar trends in the percent departure were observed over the measured temperature ranges. The surface tensions of molten KNO_3 were also remeasured periodically, and in each case the agreement was well within a reasonable experimental error ($\pm 0.30 \times 10^{-3}$ N m^{-1}, ca. ±0.3%). These mean that the apparatus is reliable enough to evaluate the surface tension of molten salts with low melting points.

Electrical Conductivity. A conventional ac bridge method was used to measure resistance of the melt in addition to that measured in previous investigation (*20*). A variable capacitance was also introduced in a Wheatstone bridge arrangement to correct the capacity of the electrical double layer near the electrode surface. A block diagram of the conductivity ac-

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