Electrical Conductances of the Molten $NaPO_3$-$Na_4P_2O_7$ System

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Electrical conductance measurements are given on four sodium polyphosphate melts in the region 1.16 $\leqq$ (Na_2O/P_2O_5) $\leqq$ 1.48, in the temperature range from the liquidus to over 850° C, and these results are correlated with available literature density and viscosity data.

THE study of transport properties can produce information about the structure and mechanisms of ionic motion in fused salt systems.

EXPERIMENTAL

Reagent grade $NaPO_3$ and $Na_4P_2O_7\cdot 10H_2O$ were obtained from the Baker and Adamson Co. The $Na_4P_2O_7\cdot 10H_2O$ was dehydrated as completely as possible by heating in a porcelain casserole over a burner for ca. 2 hours. This sample, as well as the $NaPO_3$, was oven-dried at ca. 130° C for an additional 72 hours. The samples were cooled in a Drierite desiccator before being used. It was established earlier by accurate pre- and postweighings that this procedure quantitatively converted the decahydrate to $Na_4P_2O_7$.

The Vycor conductivity cell used was similar in construction to the borosilicate one employed by Copeland and Zybko (*4*). Its over-all length was 12.7 cm, and its arms rested on a 250-ml Vycor beaker, which contained the melt. The cell contained a 2-mm-i.d. capillary 7.62 cm long, positioned horizontally in the melt in the form of an arc. The Chromel-Alumel thermocouple junction (protected by a Vycor sheath), conductance electrodes (of 24-gage Pt wire), and capillary all lay in the same horizontal plane to eliminate the effect of any vertical temperature gradient. The thermocouple was calibrated at the following reference points: freezing point of water (0° C), boiling point of water at the current barometric pressure, boiling point of benzophenone (306° C), and freezing point of NaCl (801° C). The cell constant, determined using conductance data for molten $NaNO_3$ over a temperature interval to 500° C (*5*), was 166.0 cm^{-1} and temperature-independent. It was assumed that this temperature independence of the Vycor held at the higher temperatures employed for the polyphosphate work.

The electrical resistance furnace used had a 4-inch-diameter aluminum oxide core and was equipped with a stainless steel sleeve of 3/16-inch walls and bottom to improve heat distribution. Argon was passed continuously from the bottom through the furnace to provide an inert environment.

Conductivity measurements were made with a Leeds & Northrup No. 4660 Jones-type bridge. A Heathkit Model IG-82 sine wave generator provided a 1000-Hz signal. Stray capacitance was balanced by an Industrial Instruments Co. Model DK2A decade capacitance box. Null detection was provided by a laboratory-constructed band-pass amplifier, and Tektronix Type 545A oscilloscope with a Type K plug-in preamplifier unit. Shielded cable was used throughout, except between the cell and the bridge. The steel furnace sleeve was electrically grounded.

The study began with the melt composition of lowest Na_2O/P_2O_5 mole ratio. The equilibration of the system at a particular temperature or composition was followed by conductance measurements. Upon attainment of equilibrium, conductance measurements were made at small temperature intervals, in each instance allowing the system to reach thermal equilibrium over a period of at least 3 to 4 hours. New melt compositions were obtained by adding the required amount of $Na_4P_2O_7$ to the existing melt to obtain the desired Na_2O/P_2O_5 ratio. Resistance measurements were made on the various melt compositions over a temperature range of at least 100°. The measurements were found to be reproducible in returning to particular temperatures after a time lapse of days. No noticeable attack on the Vycor was observed in the time interval of the experiment.

RESULTS AND DISCUSSION

Specific conductances were calculated by the formula

$$\kappa = C/R \tag{1}$$

where C is the cell constant and R is the resistance in ohms. The equivalent conductances were calculated using the relation

$$\Lambda = M\kappa/\rho \tag{2}$$

where M is the equivalent weight of the melt and ρ is its density. Values of the latter were computed from the empirical equation (*3*)

$$\rho = 2.372 + 0.089\ (Na_2O/P_2O_5) - 0.000338t\ (\pm 0.2\%) \tag{3}$$

where t is temperature in ° C.

Figure 1 consists of plots of log Λ *vs.* $1/T$, in $(°K)^{-1}$. Table I summarizes these conductance results. Figure 2 shows plots of Λ *vs.* composition, and Figure 3 is a graph of the so-called equivalent conductance "activation energy," as defined by the equation

$$E_\Lambda = -R[\mathrm{d}\ \ln\Lambda/\mathrm{d}(1/T)]_P \tag{4}$$

vs. composition.

Viscosities of the molten polyphosphate mixtures at the various temperatures were calculated using the equation obtained by Callis *et al.* (*2*)

$$\eta = A\ \exp\ (E_\eta/RT) \tag{5}$$

in which it was found that

$$\log E_\eta = -0.515(Na_2O/P_2O_5) + 4.722 \tag{6}$$

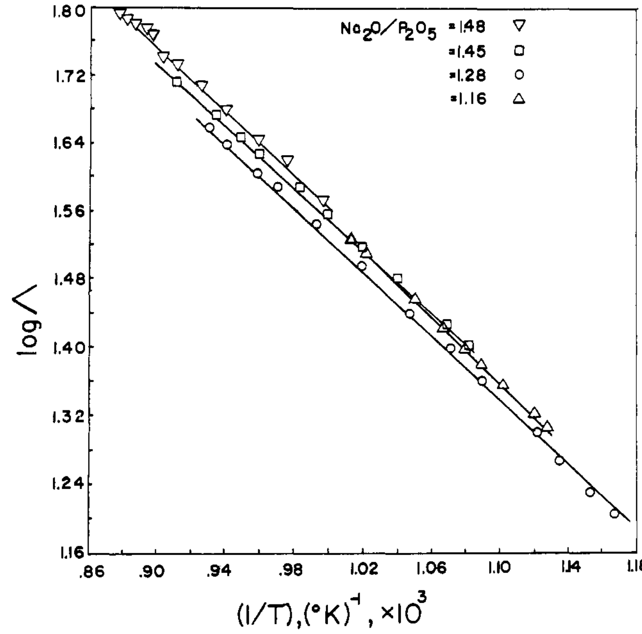

Figure 1. Common log of equivalent conductance of fused polyphosphate mixtures, log Λ, *vs.* reciprocal absolute temperature, $1/T$

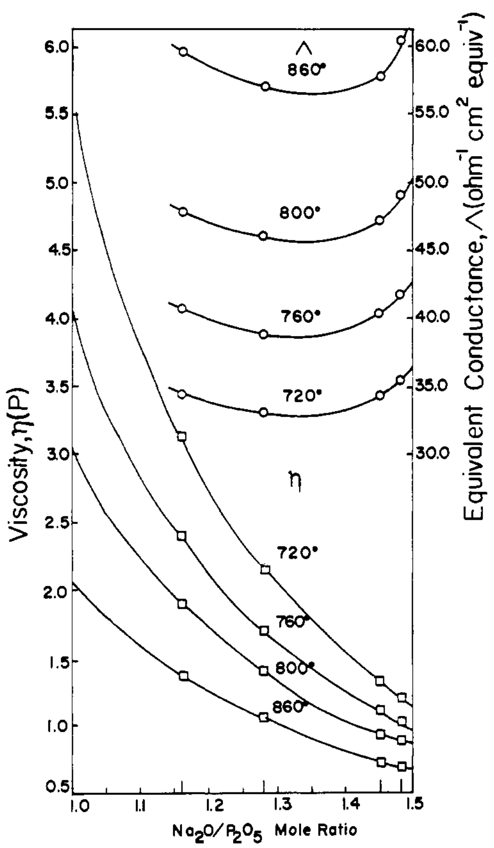

Figure 2. Equivalent conductance, Λ, and viscosity, η, isotherms *vs.* composition in terms of Na_2O/P_2O_5 ratio

and

$$A = 0.0298(Na_2O/P_2O_5)^2 - 0.0522(Na_2O/P_2O_5) + 0.0240 \quad (7)$$

Callis *et al.* claim the deviations of the melt from these empirical relations to range from −3 to 6% in E_η, and from −7 to 10% in A. Figure 2 also contains plots of η *vs.* composition, and Figure 3 also shows a plot of the apparent activation energy for viscous flow, E_η, *vs.*

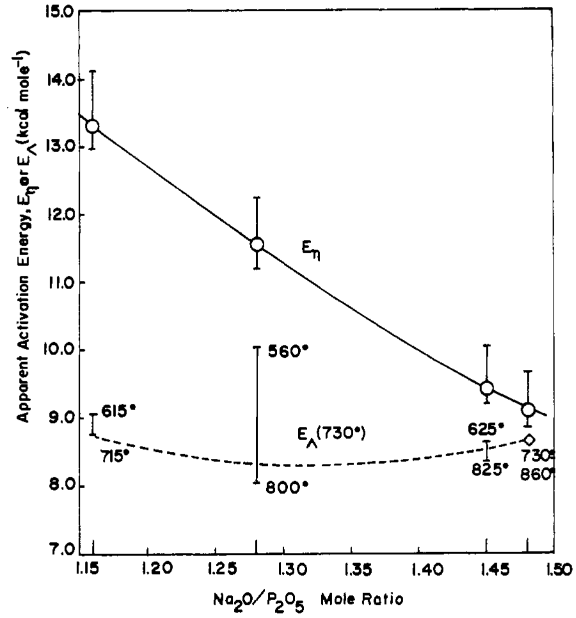

Figure 3. Apparent activation energies for equivalent conductance, E_Λ, and for viscosity, E_η, *vs.* composition in terms of Na_2O/P_2O_5 ratio

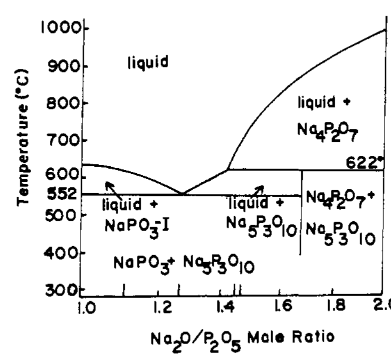

Figure 4. Sodium phosphate phase diagram for compositions between $2Na_2O/P_2O_5$ and Na_2O/P_2O_5

Compositions studied marked on abscissa at Na_2O/P_2O_5 = 1.16, 1.28, 1.45, and 1.48

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composition. Data for these plots were deduced from the equations of Callis *et al.* (Equations 5, 6, and 7) and were not determined in the present work. Calculated apparent Walden products, $\Lambda\eta$, are tabulated in Table I.

Figure 4 is the temperature-composition phase diagram of the polyphosphate system (7). The Na_2O/P_2O_5 ratios of 1.16, 1.28, 1.45, and 1.48 investigated in the present work are marked at the appropriate points on the abscissa.

A larger scale plot of the data of Figure 1 shows a distinct curvature in the line for Na_2O/P_2O_5 = 1.28—i.e., the eutectic composition. This may be meaningful, and is reflected qualitatively in Figure 3 by the spread for the value of E_Λ at Na_2O/P_2O_5 = 1.28.

The minimum in each isotherm of Λ may be of interest, particularly in comparison with a possible high conductivity at Na_2O/P_2O_5 = 2.0, ($Na_4P_2O_7$), from extrapolation. The true interpretation, however, is not likely to be a simple one [a very similar minimum appears in the simpler KCl-LiCl system of Van Artsdalen and Yaffe (6)].

For most molten salt systems Walden's law is not even qualitatively applicable, apparently because of the difference

Table I. Electrical Conductances and Walden Products for $NaPO_3$-$Na_4P_2O_7$ Melts

$(Na_2O/P_2O_5) = 1.16$, M.P. = 610° C

t, ° C	κ, Ohm^{-1} Cm^{-1}	Λ, Ohm^{-1} Cm^2	Λη
615.4	0.4992	20.35	140
616.4	0.5009	20.32	139
620.2	0.5134	20.85	138
622.2	0.5181	21.04	137
625.8	0.5287	21.49	135
631.8	0.5457	22.20	133
636.1	0.5597	22.78	132
638.1	0.5637	22.95	131
640.4	0.5726	23.32	130
646.0	0.5920	24.12	129
650.0	0.6021	24.56	127
651.7	0.6085	24.82	127
653.2	0.6146	25.08	127
656.3	0.6271	25.60	126
659.2	0.6316	25.79	125
660.1	0.6312	25.78	124
668.8	0.6629	27.11	121
679.6	0.6978	28.59	118
679.8	0.6986	28.62	118
683.2	0.7058	28.93	117
689.0	0.7281	29.87	115
698.1	0.7580	31.14	113
702.9	0.7775	31.97	112
706.8	0.7878	32.41	110
709.7	0.7965	32.78	109
715.0	0.8157	33.60	108

$(Na_2O/P_2O_5) = 1.28$, M.P. = 552° C

t, ° C	κ, Ohm^{-1} Cm^{-1}	Λ, Ohm^{-1} Cm^2	Λη
559.6	0.3526	13.27	87.6
561.6	0.3594	13.53	87.7
571.9	0.3885	14.65	87.3
578.2	0.4015	15.15	85.8
585.1	0.4239	16.02	85.9
595.5	0.4507	17.05	84.2
596.0	0.4529	17.13	84.4
608.7	0.4894	18.56	83.0
612.5	0.5026	19.06	82.9
643.1	0.5946	22.65	79.1
652.0	0.6257	33.87	78.3
661.6	0.6590	25.19	77.6
675.5	0.6992	26.77	75.2
675.8	0.7034	26.93	75.4
676.0	0.6995	26.78	75.0
677.7	0.7131	27.31	75.6
682.7	0.7255	27.82	74.6
708.8	0.8157	31.40	71.6
735.1	0.9131	35.27	69.1
737.3	0.9156	35.39	68.3
759.7	0.9970	38.66	66.1
770.1	1.035	40.21	64.7
791.9	1.118	43.58	62.8
803.9	1.169	43.65	61.6

$(Na_2O/P_2O_5) = 1.45$, M.P. = 628° C

t, ° C	κ, Ohm^{-1} Cm^{-1}	Λ, Ohm^{-1} Cm^2	Λη
628.6	0.6222	21.94	46.7
633.2	0.6382	22.53	46.9
652.7	0.7100	25.14	46.8
664.0	0.7504	26.61	46.6
670.2	0.7632	27.09	45.8
674.1	0.7867	27.94	46.4
680.8	0.8004	28.45	45.5
690.4	0.8491	30.23	45.9
693.1	0.8548	30.45	45.7
705.3	0.8963	31.98	45.1
713.5	0.9347	33.40	45.4
715.9	0.9421	33.67	45.1
730.3	1.005	36.00	45.0
746.2	1.071	38.45	44.6
761.1	1.130	40.66	44.3
772.2	1.179	42.49	44.2
775.5	1.192	42.98	43.8
784.7	1.230	44.42	43.6
799.6	1.302	47.12	43.4
807.0	1.326	48.05	43.0
822.6	1.397	50.74	42.6
827.9	1.424	51.76	42.6

$(Na_2O/P_2O_5) = 1.48$, M.P. = 715° C

t, ° C	κ, Ohm^{-1} Cm^{-1}	Λ, Ohm^{-1} Cm^2	Λη
732.5	1.054	37.21	42.4
747.2	1.121	39.68	42.4
753.6	1.147	40.62	42.2
772.2	1.233	43.77	41.9
781.3	1.278	45.43	41.9
794.3	1.341	47.75	41.7
807.7	1.408	50.25	41.7
810.6	1.421	50.74	41.6
821.4	1.481	53.01	41.7
824.1	1.496	53.54	41.6
826.5	1.505	53.86	41.5
833.2	1.533	54.94	40.7
849.6	1.615	58.01	41.4
850.0	1.629	58.51	41.4
855.8	1.660	59.68	41.3
861.1	1.682	60.52	41.1
866.9	1.713	61.70	41.1

in mechanism between viscosity and conductance (*1*). Nevertheless, it may be of interest here that the Walden product for the polyphosphate systems shows strong trends at low Na_2O/P_2O_5 ratios, but much smaller trends at higher ratios, specifically well above the eutectic, although any interpretation should not rely on the classical Walden's law approach.

The essentially constant behavior of E_Λ, at least in the concentration range studied, indicates the insensitivity of the mobility of the Na^+ ions, which it is reasonable to presume are mainly responsible for the electrical conductance, to the change in the nature of the phosphate anions—i.e., the size or degree of polymerization. The latter structural change has been reported—e.g., from viscosity data (*2*).

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