ELECTRIC CONDUCTANCES OF AQUEOUS SOLUTIONS OF SODIUM, POTASSIUM AND AMMONIUM PEROXYDISULPHATES

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Electric conductances of aqueous solutions of sodium, potassium and ammonium peroxydisulphates were measured at temperatures 15, 20 and 25°C in the concentration range c. $2 . 10^{-4}$ N up to saturated solutions. The found values of the equivalent conductivity of peroxydisulphate ion at infinite dilution were the following: $\lambda_0 = 68\cdot6$ (15°C), $76\cdot9$ (20°C) and $85\cdot3 \ \Omega^{-1} \ cm^{-1}$ (25°C).

Data concerning the electric conductance of aqueous solutions of sodium and potassium peroxydisulphates are mostly long established[1-3] and were measured in order to determine molecular weights and consequently the chemical formulas of the mentioned substances. This is also the reason why the first two of the cited papers do not give the temperature of measurement and why the concentration dependence shows a rather great scattering of data. In further years only a single report[4] appeared on the conductance of $0\cdot001$M-$(NH_4)_2S_2O_8$ at 25°C, while the corresponding data for sodium peroxydisulphate are still lacking in the literature. Equivalent conductivity of peroxydisulphate ions, given in Tables[5], is presented without any reference to literature. Within the framework of a complete research of theoretical fundamentals of the electrolytic preparation of peroxydisulphates by anodic oxidation of the respective sulphates we have measured the electric conductances of aqueous solutions of sodium, potassium and ammonium peroxydisulphates at 15, 20 and 25°C in the concentration range c. $2 . 10^{-4}$ N up to saturated solutions.

EXPERIMENTAL

Measuring procedure. Conductance measurements were carried out on a Wheatstone bridge by determining the electric resistance of solutions of known concentration in a conductivity cell of the Jones[6] type with platinum electrodes coated with platinum black. The size of the cells was varied with respect to the concentration of the solution so that the measured resistance should lie within the range $10^2-10^3 \ \Omega$. The catalytic effect of platinum black on the spontaneous

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TABLE I

Specific ($\varkappa$) and Equivalent (λ) Conductances of Sodium, Potassium and Ammonium Peroxydisulphate Solutions at 15, 20 and 25°C

15°C

$Na_2S_2O_8$			$K_2S_2O_8$			$(NH_4)_2S_2O_8$		
val/l	$\varkappa$ $\Omega^{-1}cm^{-1}$	λ $\Omega^{-1}cm^2val^{-1}$	val/l	$\varkappa$ $\Omega^{-1}cm^{-1}$	λ $\Omega^{-1}cm^2val^{-1}$	val/l	$\varkappa$ $\Omega^{-1}cm^{-1}$	λ $\Omega^{-1}cm^2val^{-1}$
0·0001680	0·00001784	106·22	0·0001480	0·00001862	125·83	0·0001753	0·00002200	125·50
0·0003361	0·00003537	105·25	0·0002960	0·00003698	124·94	0·0003506	0·00004358	124·31
0·0006722	0·00007001	104·15	0·0005920	0·00007321	123·66	0·0007012	0·00008640	123·22
0·003361	0·0003330	99·07	0·002960	0·0003500	118·25	0·003507	0·0004112	117·24
0·01680	0·001527	90·90	0·01480	0·001595	107·75	0·01754	0·001905	108·66
0·06720	0·005469	81·38	0·05919	0·005626	95·05	0·07012	0·006872	98·01
0·1680	0·01230	73·24	0·1480	0·01225	84·81	0·1753	0·01575	89·82
0·3360	0·02253	67·05	0·2758[a]	0·02166[a]	78·54[a]	0·3505	0·02952	84·21
0·8528	0·04825	56·58	—	—	—	0·8770	0·06721	76·64
1·7588	0·08069	45·88	—	—	—	1·7539	0·1224	69·79
2·9815	0·1037	34·78	—	—	—	2·6414	0·1740	66·12
4·5334	0·1064	23·47	—	—	—	4·3893	0·2353	53·60
4·5839[a]	0·1053[a]	22·97[a]	—	—	—	4·7415[a]	0·2399[a]	50·60[a]

20°C

$Na_2S_2O_8$			$K_2S_2O_8$			$(NH_4)_2S_2O_8$		
val/l	$\varkappa$ $\Omega^{-1}cm^{-1}$	λ $\Omega^{-1}cm^2val^{-1}$	val/l	$\varkappa$ $\Omega^{-1}cm^{-1}$	λ $\Omega^{-1}cm^2val^{-1}$	val/l	$\varkappa$ $\Omega^{-1}cm^{-1}$	λ $\Omega^{-1}cm^2val^{-1}$
0·0001680	0·00002006	119·41	0·0001480	0·00002085	140·92	0·0001753	0·00002466	140·72
0·0003360	0·00003976	118·35	0·0002963	0·00004144	139·81	0·0003506	0·00004898	139·69
0·0006721	0·00007859	116·93	0·0005929	0·00008194	138·20	0·0007011	0·00009712	138·52
0·003361	0·0003750	111·59	0·002960	0·000393	132·76	0·003507	0·0004652	132·65
0·01680	0·001718	102·23	0·01480	0·001791	120·97	0·01754	0·002146	122·35
0·06720	0·006131	91·24	0·05919	0·006309	106·57	0·07012	0·007707	109·91
0·1680	0·01377	81·96	0·1480	0·01407	95·09	0·1753	0·01759	100·33
0·3360	0·02525	75·16	0·2960	0·02566	86·70	0·3505	0·03313	94·53

25°C

0·8517	0·05498	64·55	0·3506ᵃ	0·03007ᵃ	85·77ᵃ	0·8764	0·07476	85·30
1·7542	0·09172	52·29	—	—	—	1·7528	0·1362	77·70
2·9755	0·1175	39·49	—	—	—	2·6291	0·1922	73·10
4·5163	0·1215	26·90	—	—	—	4·3819	0·2588	59·06
4·7118ᵃ	0·1199ᵃ	24·45ᵃ	—	—	—	4·960ᵃ	0·2674ᵃ	53·91ᵃ
0·0001680	0·00002229	132·71	0·0001480	0·00002306	155·87	0·0001753	0·00002739	156·25
0·0003361	0·00004420	131·49	0·0002959	0·00004576	154·66	0·0003506	0·00005465	155·60
0·0006714	0·00008730	130·02	0·0005922	0·00009074	153·22	0·0007016	0·0001080	153·90
0·003362	0·0004170	124·02	0·002960	0·0004355	147·12	0·003508	0·0005175	147·52
0·01681	0·001910	113·64	0·01480	0·001985	134·13	0·01754	0·002385	136·07
0·06720	0·006809	101·32	0·05919	0·006987	118·05	0·07011	0·008586	122·46
0·1680	0·01535	91·35	0·1480	0·01569	106·05	0·1753	0·01964	112·05
0·3360	0·02810	83·63	0·2959	0·02849	96·28	0·3506	0·03679	104·94
0·8506	0·06026	70·84	0·4395ᵃ	0·04015ᵃ	91·35ᵃ	0·8751	0·08231	94·06
1·7524	0·1008	57·52				1·7508	0·1491	85·16
2·9686	0·1309	44·09				2·6266	0·2097	79·84
4·5129	0·1363	30·20				4·3737	0·2813	64·32
4·8283ᵃ	0·1328ᵃ	27·50ᵃ				5·2198ᵃ	0·2929ᵃ	56·11ᵃ

ᵃ Saturated solution.

decomposition of peroxydisulphate ions was eliminated by using cells with coating at least one month old in which the stock solution of peroxydisulphate had been kept. In these cells the electric resistance of the solutions measured at constant temperature did not change for 10 min at minimum. Conductivity cells were placed in a thermostat filled with distilled water and maintained at the desired temperature with the accuracy of $\pm 0.03°C$. The remaining arrangement and the measuring procedure were the same as described in the previous paper[7].

Chemicals used. Potassium and ammonium peroxydisulphates were prepared by repeated recrystallisation of the commercial chemicals of the reagent grade purity from distilled water in the temperature interval 50—0°C. Sodium peroxydisulphate was prepared from ammonium peroxydisulphate, purified in the above described way, by conversion with a 50% solution of sodium hydroxide, free of carbonates, under cooling and in a stream of nitrogen[8]. Solutions of the desired concentration were prepared by dissolving weighted amounts of the purified salts in redistilled water which was obtained by three-fold distillation of normal distilled water, and by filling up to the appropriate volume. Conductivity of the used redistilled water was $2.2 . 10^{-7}$ (15°C), $2.4 . 10^{-7}$ (20°C) and $2.6 . 10^{-7} \Omega^{-1} cm^{-1}$ (25°C). Concentration of the measured solutions ranged from c. $2 . 10^{-4}N$ up to saturated solutions whose composition is given in papers[8–10].

RESULTS AND DISCUSSION

We performed at least three measurements for each concentration, always with freshly prepared solutions. Mean values of the data obtained in this manner were plotted as the dependence of λ *vs* $c^{1/2}$ with graphical smoothing. Deviations of the smoothed values from the measured ones varied within $\pm 0.3\%$ rel. The found specific and equivalent conductivities of solutions of individual peroxydisulphates are summarized in Table I. The measured values of equivalent conductivities for highly diluted solutions were used to determine, using Owen's method[11], equivalent conductivities for infinite dilution λ_0, from the graphical dependence of the quantity $(\lambda - \lambda_0 + S . c^{1/2})/c$ on $\log c$, which, for an appropriately chosen value of λ_0 shows a linear course. S is the slope in the Onsager's limiting relation and it can be calculated from the expression[12]

$$S = [a'' . q\lambda_0/(1 + q^{1/2})] + b'' , \qquad (1)$$

where q is defined for an uni-bivalent electrolyte by the relation

$$q = 2\lambda_0/[3(\lambda_0 + \lambda_{10})] . \qquad (2)$$

λ_0 is the equivalent conductivity of the electrolyte at infinite dilution and λ_{10} is the corresponding conductivity of the univalent cation of the electrolyte. The values of a'' and b'' for the given type of electrolyte were calculated from the relations of the Debye–Hückel model

$$a'' = 2e^3|z_1 z_2| [\pi N(|z_1| + |z_2|)]^{0.5}/3(10\varepsilon kT)^{1.5} , \qquad (3)$$

$$b'' = e^3 [N(|z_1| + |z_2|)]^{1.5} / 3\eta (10^3 \pi \varepsilon k T)^{0.5} \qquad (4)$$

and their actual values for different temperatures are presented in Table II.

TABLE II

Values of the Constants Used to Determine $\lambda_{0,M_2S_2O_8}$ according to Owen's Method and Values of $\lambda_{0,exp}$ of individual Peroxydisulphates

Quantity	15°C	20°C	25°C
a''	1·881	1·898	1·915
b''	86·3	98·2	110·8
λ_{0,Na^+}	39·77	44·85	50·12
λ_{0,K^+}	59·66	66·44	73·50
λ_{0,NH_4^+}	59·60	66·44	73·55
$\lambda_{0,expNa_2S_2O_8}$	108·8	121·8	135·5
$\lambda_{0,expK_2S_2O_8}$	127·9	143·4	158·6
$\lambda_{0,exp(NH_4)_2S_2O_8}$	128·1	143·2	158·9

TABLE III

Values of Equivalent Conductivity and of Diffusion Coefficient of the Peroxydisulphate Ion and Equivalent Conductivities of Peroxydisulphates at Infinite Dilution at 15, 20 and 25°C

t, °C	$\lambda_{0,S_2O_8^{2-}}$ determined from the data for			$\lambda_{0,S_2O_8^{2-}}$
	$\lambda_{0,expNa_2S_2O_8}$	$\lambda_{0,expK_2S_2O_8}$	$\lambda_{0,exp(NH_4)_2S_2O_8}$	
15	69·0	68·2	68·5	68·6 ± 0·4
20	77·0	77·0	76·7	76·9 ± 0·2
25	85·4	85·10	85·4	85·3 ± 0·2

$\lambda_{0,Na_2S_2O_8}$	$\lambda_{0,K_2S_2O_8}$	$\lambda_{0,(NH_4)_2S_2O_8}$	$D_{0,S_2O_8^{2-}} \cdot 10^5$ $cm^2 \cdot s^{-1}$
108·4	128·3	128·2	0·883
121·8	143·3	143·3	1·007
135·4	158·8	158·8	1·136

Equivalent conductivities of the peroxydisulphate anion $\lambda_{0,S_2O_8^{2-}}$ were then calculated from the equivalent conductivities λ_0 of individual peroxydisulphates, using the data of equivalent conductivities for different cations. The values of equivalent conductivities of cations at infinite dilution were taken from the book of Robinson and Stokes[13], either directly or by interpolation of the data published therein, and are also summarized in Table II. Table III gives the values of $\lambda_{0,S_2O_8^{2-}}$, as determined in the measurements of individual peroxydisulphates. The mean values of this quantity (see also Table III) and of the equivalent conductivities of individual cations were used to calculate the most probable values of equivalent conductivities of the studied peroxydisulphates at infinite dilution which are also included in Table III as λ_0.

Temperature dependence of the equivalent conductivity of the peroxydisulphate anion at infinite dilution $\lambda_{0,S_2O_8^{2-}}$ can be expressed in the temperature interval 15 to 25°C with sufficient accuracy by the following relation

$$\lambda_{0,S_2O_8^{2-}} = \lambda_{0,S_2O_8^{2-},\,25°C}\left[1 - 0.0196(25 - t)\right], \tag{5}$$

or

$$\lambda_{0,S_2O_8^{2-},\,t} = \lambda_{0,S_2O_8^{2-},\,25°C} - 1.67(25 - t). \tag{5a}$$

In the mentioned interval the temperature gradient of the equivalent conductivity of peroxydisulphate ion at infinite dilution is almost identical with the temperature gradient of sulphate ion, the experimental value[14] of which for λ_0 in the interval $18-25°C$ can also be fitted with a straight line with the slope 1.66 (if the dependence is expressed in the form of equation (5a). It is also possible to calculate the diffusion coefficient of peroxydisulphate ion at infinite dilution from the values of equivalent conductivities at infinite dilution, according to the relation $D_0 = RT\lambda_0/|z|\,F^2$ (see also Table III).

From Figs 1 and 2, showing the dependence of specific conductivity of aqueous solutions of peroxydisulphates on their equivalent concentration, it is evident that the conductivity of potassium salt increases steadily with increasing concentration, owing to its limited solubility. With sodium salt, whose solubility is by more than one order of magnitude higher than that of potassium salt, a conductivity maximum appears at all temperatures. Its position shifts with increasing temperature towards higher concentrations. In the case of ammonium salt, which is still more soluble than the sodium salt, no maximum can be seen at any temperature, although it cannot be excluded, from the course of the dependences, that the conductivity of saturated solutions of this salt might approach a maximum very closely. The presented results can be applied e.g. to determine the appropriate concentration of initial solutions in the electrolytic preparation of peroxydisulphates, which should lead to final solu-

tions with the highest possible conductance and consequently to the lowest values of the ohmic voltage drop within the electrolyte[7].
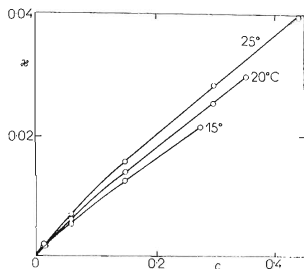

FIG. 1

Dependence of Specific Conductivity $\varkappa$ (Ω^{-1} cm^{-1}) of Potassium Peroxydisulphate on Concentration (val/l) at 15°, 20° and 25°C
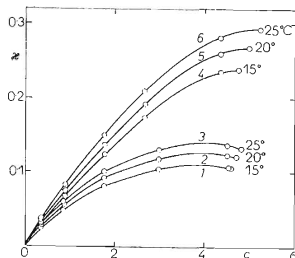
FIG. 2

Dependence of Specific Conductivity $\varkappa$ (Ω^{-1} cm^{-1}) of Sodium (1, 2, 3) and Ammonium (4, 5, 6) Peroxydisulphate on Concentration (val/l) at 15°, 20° and 25°C

Comparison of the measured data with the hitherto published ones revealed that the values given by Moeller[3] for potassium peroxydisulphate at 25°C are throughout lower than our results. The comparison with the data obtained by Marshall[1] and Bredig[2] is impossible, because these authors do not give the temperature of measurement. Contrary to this, the single value of King[4] for 0·001M-(NH$_4$)$_2$S$_2$O$_8$ at 25°C is a little higher than our value. The value of $\lambda_{0,S_2O_8^{2-}, 25°C} = 86\ \Omega^{-1}$ cm^{-1} val^{-1} in the Tables[5] is in fairly good agreement with the value found in our measurements.

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