Properties of aqueous solutions of sulfamic acid and of some sulfamates

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RIASSUNTO - *PROPRIETA' DELLE SOLUZIONI ACQUOSE DI ACIDO SOLFAMMICO E DI ALCUNI SUOI SALI* - Si sono determinate: densità, viscosità, tensione superficiale e conducibilità delle soluzioni acquose di acido solfammico e di alcuni suoi sali di interesse applicativo.

SUMMARY - Density, viscosity, surface tension and conductivity of aqueous solutions of sulfamic acid and of some sulfamates have been determined.

The lack of data concerning the chemical-physical and electrochemical properties of the sulfamate baths (1) suggested a systematic investigation of some of them, especially interesting also in view of the applications and in particular: density, viscosity, surface tension, electrical conductivity.

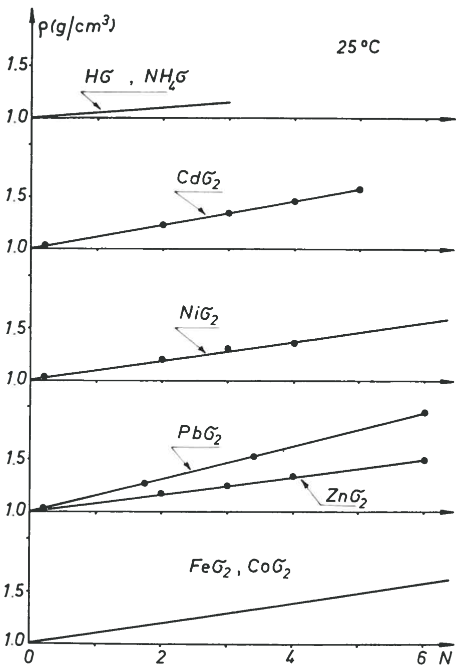

Fig. 1 Density of aqueous solutions of Hσ and some salts as a function of normality.

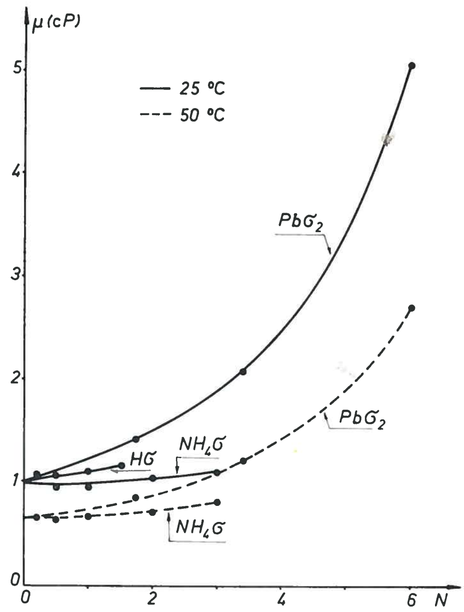

Fig. 2 Viscosity of aqueous solutions of Hσ, $NH_4σ$ and $Pbσ_2$, as a function of normality and temperature.

TABLE 1

Density (g/cm³) of aqueous solutions of sulfamic acid and some salts as a function of temperature θ (°C) and normality N.

Y	θ \ N	0.01	0.05	0.1	0.2	0.4	0.5	1	1.5	2	3	4	5	6
Hσ	25	1.00	1.00	1.00	—	—	1.025	1.050	1.075	—	—	—	—	—
$NH_4σ$	25	—	—	—	1.015	—	1.035	1.060	—	1.105	1.150	—	—	—
$Pbσ_2$	25	—	—	—	1.040	—	—	—	—	1.280 *	1.530 **	—	—	1.960
$Cdσ_2$	25	—	—	—	1.030	—	—	—	—	1.235	1.340	1.450	1.570	—
$Znσ_2$	25	—	—	—	1.030	—	—	—	—	1.180	1.255	1.330	—	1.485
$Feσ_2$	25	—	—	—	—	1.030	—	1.075 ***	—	1.220 ****	—	1.375	—	—
$Niσ_2$	25	—	—	—	1.030	—	—	—	—	1.205	1.290	1.365	—	1.600 *****
$Coσ_2$	25	—	—	—	1.025	—	—	—	—	1.205	1.266	1.385	—	1.554
	50	—	—	—	1.015	—	—	—	—	1.200	1.265	—	—	1.553
	75	—	—	—	0.980	—	—	—	—	1.190	1.255	—	—	—

* N = 1.75; ** N = 3.42; *** N = 0.90; **** N = 2.30; ***** N = 6.6.

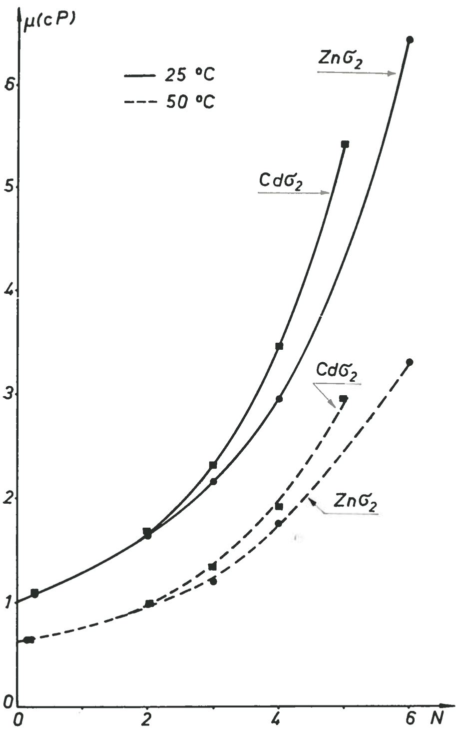

Fig. 3 Viscosity of aqueous solutions of $Cd\sigma_2$, $Zn\sigma_2$.

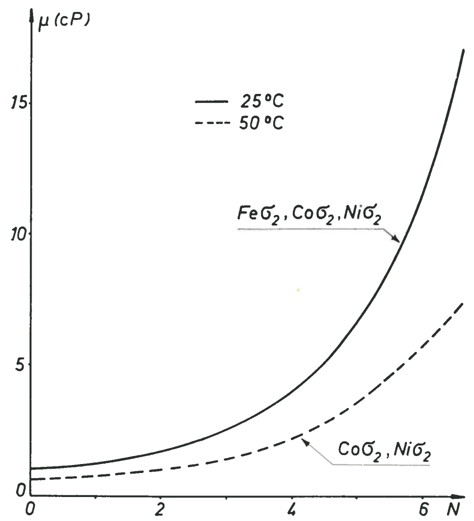

Fig 4 Viscosity of aqueous solutions of $Fe\sigma_2$, $Co\sigma_2$, $Ni\sigma_2$.

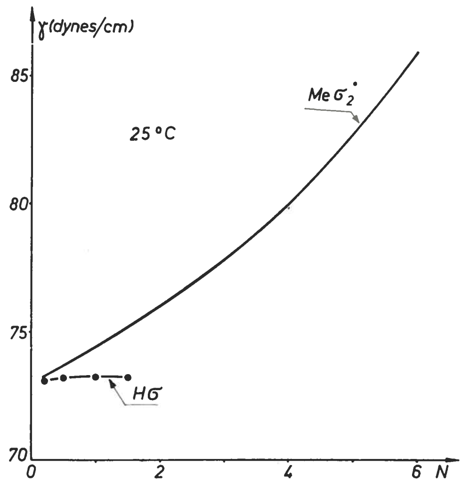

Fig. 5 Surface tension of aqueous solutions of $H\sigma$ and some salts as a function of normality. Me = Pb, Cd, Zn, Ni, Co, $(NH_4)_2$.

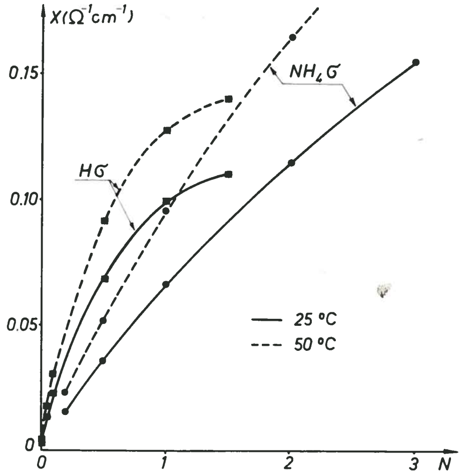

Fig. 6 Conductivity of aqueous solutions of $H\sigma$ and $NH_4\sigma$ as a function of normality and temperature.

Experimental and results

The density measures have been carried out by aereometry. The other measurements have been carried out by means of: an Ubbelohde viscometer * (2), a Trau-

* The calibration of the apparatus gave: $\nu = 0.00999$ t (ν being the kinematic viscosity (cSt) and t (sec) the efflux time.

TABLE 2

Viscosity (cP) of aqueous solutions of sulfamic acid and some salts as a function of temperature (°C) and normality.

Y	θ \ N	0.01	0.05	0.1	0.2	0.4	0.5	1	1.5	2	3	4	5	6
Hσ	25	1.00	1.00	1.01	—	—	1.06	1.10	1.155	—	—	—	—	—
$NH_4σ$	25	—	—	—	0.945	—	0.94	0.955	—	1.03	1.11	—	—	—
	50	—	—	—	0.64	—	0.63	0.67	—	0.72	0.805	—	—	—
$Pbσ_2$	25	—	—	—	1.08	—	—	—	—	1.42 *	2.07 **	—	—	5.06
	50	—	—	—	0.658	—	—	—	—	0.855 *	1.21 **	—	—	2.68
$Cdσ_2$	25	—	—	—	1.07	—	—	—	—	1.71	2.33	3.45	5.38	—
	50	—	—	—	0.64	—	—	—	—	1.01	1.34	1.88	2.95	—
$Znσ_2$	25	—	—	—	1.07	—	—	—	—	1.64	2.15	2.94	—	6.4
	50	—	—	—	0.65	—	—	—	—	0.99	1.20	1.75	—	3.3
$Feσ_2$	25	—	—	—	—	1.15	—	1.21 ***	—	1.96 ****	—	3.85	—	—
$Niσ_2$	25	—	—	—	1.07	—	—	—	—	1.76	2.40	3.75	—	17.0 *****
	50	—	—	—	0.65	—	—	—	—	1.025	1.46	2.06	—	7.0 *****
$Coσ_2$	25	—	—	—	1.06	—	—	—	—	1.74	2.60	4.11	—	11.2
	50	—	—	—	0.64	—	—	—	—	1.02	1.46	2.22	—	6.1

* N = 1.75; ** N = 3.42; *** N = 0.90; **** N = 2.30; *****N = 6.6.

TABLE 3

Surface tension (dynes/cm) of aqueous solutions of sulfamic acid and some salts as a function of normality.

Y	θ \ N	0.01	0.05	0.1	0.2	0.5	1	1.5	2	3	4	5	6
Hσ	25	72.75	72.75	72.75	—	73.2	73.2	73.2	—	—	—	—	—
$NH_4\sigma$	25	—	—	—	73.2	74.2	75.0	—	76.8	78.5	—	—	—
$Pb\sigma_2$	25	—	—	—	73.5	—	—	—	75.5 *	78.5 **	—	—	84.0
$Cd\sigma_2$	25	—	—	—	73.5	—	—	—	76.5	78	80.5	83.0	—
$Zn\sigma_2$	25	—	—	—	74.0	—	—	—	75.2	77.7	79.1	—	84.5
$Ni\sigma_2$	25	—	—	—	73.0	—	—	—	77.0	78.8	80.0	—	89.5 ***
$Co\sigma_2$	25	—	—	—	72.6	—	—	—	76.5	76.6	80.5	—	87.9

* N = 1.75; ** N = 3.42; *** N = 6.6.

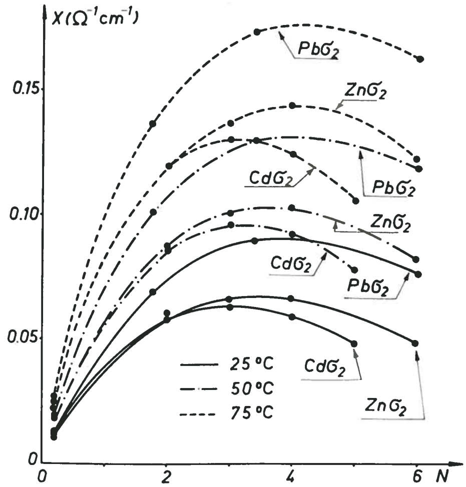

Fig. 7 Conductivity of aqueous solutions of $Pb\sigma_2$, $Cd\sigma_2$, $Zn\sigma_2$.

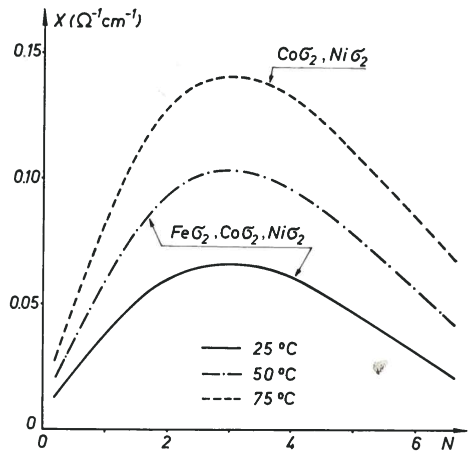

Fig. 8 Conductivity of aqueous solutions of $Fe\sigma_2$, $Co\sigma_2$, $Ni\sigma_2$.

be stalagmometer * (3) and a Jones conductivity bridge **.

At 25 °C, the density of the sulfamic solutions increases with a nearly linear law,

* The calibration, at 25 °C, of the apparatus gave: $\gamma = 1875 \frac{\rho}{N}$, γ (dynes/cm) being the surface tension; ρ (g/cm³) che density and N the number of drops leaving the stalagmometer, in correspondence to a given volume change of the inner liquid.

** Bridge approximation: ± 2.02%. Cell constant: 0.572 (cm^{-1}).

TABLE 4

Conductivity (Ω^{-1} cm^{-1}) of aqueous solutions of sulfamic acid and some salts as a function of temperature (°C) and normality.

Y	θ \ N	0.01	0.05	0.1	0.2	0.4	0.5	1	1.5	2	3	4	5	6
Hσ	25	0.0033	0.0133	0.0231	—	—	0.0682	0.0989	0.1100	—	—	—	—	—
	50	0.0044	0.0178	0.0310	—	—	0.0910	0.1275	0.1400	—	—	—	—	—
$NH_4\sigma$	25	—	—	—	0.0156	—	0.0357	0.0659	—	0.1145	0.1550	—	—	—
	50	—	—	—	0.0232	—	0.0525	0.0955	—	0.1640	0.2200	—	—	—
$Pb\sigma_2$	25	—	—	—	0.0129	—	—	—	—	0.0690 *	0.0895 **	—	—	0.0762
	50	—	—	—	0.0194	—	—	—	—	0.1011 *	0.1297 **	—	—	0.1190
	75	—	—	—	0.0268	—	—	—	—	0.1365 *	0.1735 **	—	—	0.1635
$Cd\sigma_2$	25	—	—	—	0.0117	—	—	—	—	0.0585	0.0630	0.0590	0.0485	—
	50	—	—	—	0.0181	—	—	—	—	0.0855	0.0955	0.0925	0.0783	—
	75	—	—	—	0.0250	—	—	—	—	0.1190	0.1297	0.1245	0.1060	—
$Zn\sigma_2$	25	—	—	—	0.0107	—	—	—	—	0.0579	0.0651	0.0659	—	0.0480
	50	—	—	—	0.0165	—	—	—	—	0.0869	0.1005	0.1020	—	0.0819
	75	—	—	—	0.0220	—	—	—	—	0.1195	0.1360	0.1435	—	0.1220
$Fe\sigma_2$	25	—	—	—	—	0.0196	—	0.0365 ***	—	0.0610 ****	—	0.0602	—	—
	50	—	—	—	—	0.0293	—	0.0550 ***	—	0.0955 ****	—	0.0938	—	—
$Ni\sigma_2$	25	—	—	—	0.0121	—	—	—	—	0.0590	0.0635	0.0595	—	0.0244 *****
	50	—	—	—	0.0186	—	—	—	—	0.0910	0.0988	0.0955	—	0.0447 *****
	75	—	—	—	0.0254	—	—	—	—	0.1245	0.1365	0.1297	—	0.0699 *****
$Co\sigma_2$	25	—	—	—	0.0130	—	—	—	—	0.0625	0.0682	0.0610	—	0.0273
	50	—	—	—	0.0205	—	—	—	—	0.0989	0.1061	0.0972	—	0.0540
	75	—	—	—	0.0265	—	—	—	—	0.1335	0.1435	0.1335	—	0.0830

* N = 1.75; ** N = 3.42; *** N = 0.90; **** N = 2.30; ***** N = 6.6.

when normality increases (fig. 1 and tab. 1 *); its decrements by temperature increments (at constant concentration) being very small. To determining the viscosity at 50 °C, the density values at 25 °C were utilized, therefore.

Viscosity, surface tension, electric conductibility as functions of concentration and temperature are given in figures 2 to 8 and tables 2 to 4 **.

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* For brevity sake, we indicate as usual in our laboratory the group NH_2SO_3 with σ.

pH of salt solutions is always corresponding to the stoichiometric neutrality.

The properties of the copper sulfamate solutions are reported in the paper: R. Piontelli, B. Mazza, P. Pedeferri - Chemical and electrochemical behaviour of Cu(II) and Cu(I) sufamate baths and of copper against sulfamic solutions. See this volume p. 81.

** As comparison, at equality of temperature (25 °C) and normality (1.5 N) the electrical conductivity (Ω^{-1} cm^{-1}) of aqueous solutions is: $\simeq$ 0.1 for $H\sigma$, $\simeq$ 0.3 for H_2SO_4, $\simeq$ 0.4 for HCl and $\simeq$ 0.5 for $HClO_4$. The given composition is near to the saturation point at 25 °C for $H\sigma$ solutions, while for H_2SO_4, $HClO_4$ and HCl solutions conductivity increases, by increasing the concentration, till a maximum of about 0.8.

Viscosity is somewhat higher for $H\sigma$ solutions than for $HClO_4$, HCl and H_2SO_4 solutions.

Bibliography

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3. C. B. F. Young, K. W. Coons - *Surface active agents* - Chemical Publishing Co., Brooklyn (1945), chapter 2: Determination of surface tension; A. W. Adamson - *Physical chemistry of surfaces* - Interscience Publishers, New York (1960), chapter 1, § 6: The drop weight method.

Discussion

T. L. Rama Char - *Taking the conductivity data with those of the information already available on cathode polarization, one can get some idea of the throwing power of the plating solutions. The throwing power is however rather poor for all the metals, although the deposition of metals like nickel, cobalt and iron is accompanied by considerable polarization.*

Further studies are desirable to improve the throwing power.