Conductivity of the Liquid System Water + Acetic Acid + Silver Acetate

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Z. Naturforsch. **33a**, 1105–1106 (1978); received June 2, 1978

We present and discuss experimental values of the electric conductivity (and of the density) for the liquid ternary system water + acetic acid + silver acetate at 25 °C. The results given here represent a selection from measurements on more than 200 compositions. The concepts of equivalent conductivity and of limiting values for infinite dilution in the ternary system are also dealt with briefly.

We want to present and to discuss the results of measurements of the electric conductivity (and of the density) of the ternary liquid system water + acetic acid + silver acetate at 25 °C. Since our experiments were carried out for more than 200 compositions we here only give a limited amount of results. For more informations and experimental details the reader should consult the original extensive report [1].

If we stipulate that the only charged species present are H^+, Ag^+, and Ac^-, we find for the conductivity $\varkappa$:

$$\begin{aligned}\varkappa &= \sum_i |z_i|\, c_i\, \lambda_i \\ &= c_{H^+}\lambda_{H^+} + c_{Ag^+}\lambda_{Ag^+} + c_{Ac^-}\lambda_{Ac^-} \qquad (1)\\ &= \alpha_2 c_2 \lambda_{H^+} + \alpha_3 c_3 \lambda_{Ag^+} + (\alpha_2 c_2 + \alpha_3 c_3)\lambda_{Ac^-}\end{aligned}$$

where z_i denotes the charge number of ionic species i, c_i its concentration, λ_i its ionic conductivity (product of Faraday constant and mobility, water being the reference substance), and α_2 or α_3 the degree of dissociation of acetic acid (concentration c_2) or of silver acetate (concentration c_3), respectively.

Defining an "equivalent conductivity" Λ by

$$\Lambda \equiv \varkappa/(c_2 + c_3)\,, \qquad (2)$$

introducing the "equivalent fractions" X_2 and X_3 of acetic acid and silver acetate

$$X_2 \equiv c_2/(c_2+c_3)\,,$$
$$X_3 \equiv c_3/(c_2+c_3) = 1 - X_2 \qquad (3)$$

[1] H. Ben Nasr: Leitfähigkeitsmessungen am ternären System Wasser + Essigsäure + Silberacetat bei 25 °C. Diplomarbeit, Technische Hochschule Aachen, 1977.

and using the abbreviations

$$\lambda_H \equiv \alpha_2 \lambda_{H^+}\,, \quad \lambda_{Ag} \equiv \alpha_3 \lambda_{Ag^+}\,,$$
$$\lambda_{Ac} \equiv (\alpha_2 X_2 + \alpha_3 X_3)\, \lambda_{Ac^-} \qquad (4)$$

we derive from Eq. (1):

$$\Lambda = X_2 \lambda_H + X_3 \lambda_{Ag} + \lambda_{Ac}\,. \qquad (5)$$

The quantities λ_H, λ_{Ag}, and λ_{Ac} may be called the ionic conductivities of the ion constituents H, Ag, and Ac.

In Table 1 we present a selection from our experimental values of the density (required for the computation of concentrations from mass fractions), of the conductivity, and of the equivalent conductivity. Our measurements cover the range between infinite dilution and $c_2 = 0{,}5$ mol/l, $c_3 = 0{,}05$ mol/l at 25 °C. The data include values for the binary systems water + acetic acid ($c_3 = 0$) and water + silver acetate ($c_2 = 0$).

Table 1. System water + acetic acid + silver acetate at 25 °C: Density ϱ, conductivity $\varkappa$, and equivalent conductivity Λ as functions of the concentrations c_2 and c_3 of acetic acid and silver acetate.

$c_2 \cdot 10^3$ mol l^{-1}	$c_3 \cdot 10^3$ mol l^{-1}	ϱ g cm^{-3}	$\varkappa \cdot 10^4$ S cm^{-1}	Λ S cm^2 mol^{-1}
0.00	49.76	1.0034	39.40	79.19
0.00	39.82	1.0022	32.50	81.62
0.00	29.88	1.0010	25.25	84.51
0.00	19.92	0.9997	17.38	87.24
0.00	9.967	0.9984	9.25	92.80
0.00	1.994	0.9973	1.99	100.00
0.00	0.997	0.9972	1.01	101.31
415.70	49.75	1.0068	38.62	8.30
248.48	29,74	1.0029	25.23	9.07
82.97	9.93	0.9990	9.77	10.52
49.63	5.94	0.9983	6.21	11.17
26.16	3.13	0.9977	3.62	12.35
8.101	0.970	0.9973	1.47	16.21
4.044	0.484	0.9972	0.93	20.53
485.99	0.00	1.0012	10.87	2.24
390.75	0.00	1.0003	9.94	2.54
294.55	0.00	0.9995	8.71	2.96
197.37	0.00	0.9987	7.23	3.67
99.19	0.00	0.9979	5.16	5.20
9.965	0.00	0.9971	1.64	16.46
0.997	0.00	0.9971	0.486	48.75

Figures 1, 2, and 3 show plots of $\varkappa$ and Λ against $\sqrt{c_2}$ and $\sqrt{c_3}$ for the binary system water + silver acetate and for the ternary system.

For the ternary system, the limiting value of Λ for infinite dilution depends on the path of dilution.

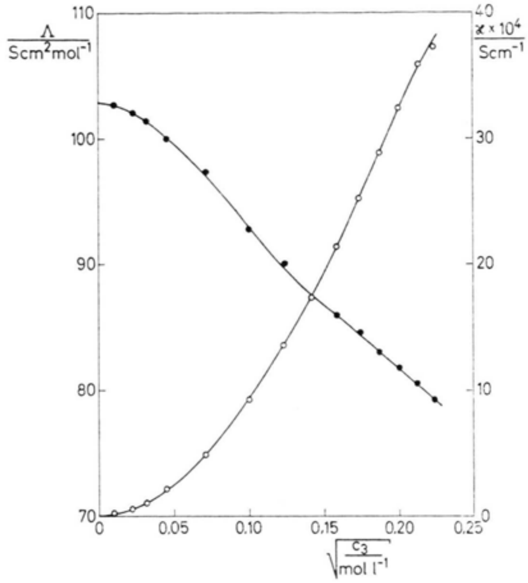

Fig. 1. Binary system water + silver acetate at 25 °C: Conductivity $\varkappa$ and equivalent conductivity Λ as functions of the square root of the concentration c_3 of silver acetate.

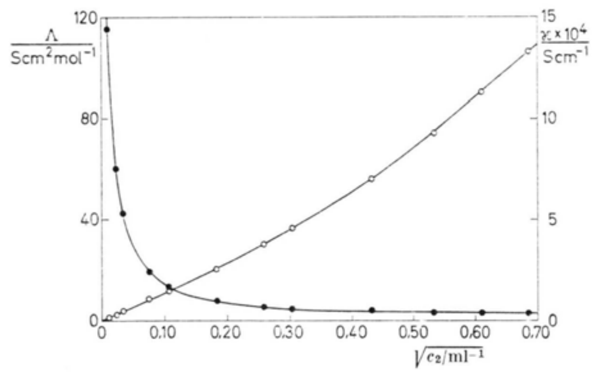

Fig. 2. Ternary system water + acetic acid + silver acetate at 25 °C: Conductivity $\varkappa$ and equivalent conductivity Λ as functions of the square root of the concentration c_2 of acetic acid for given ratio $c_3/c_2 = 0.0255$.

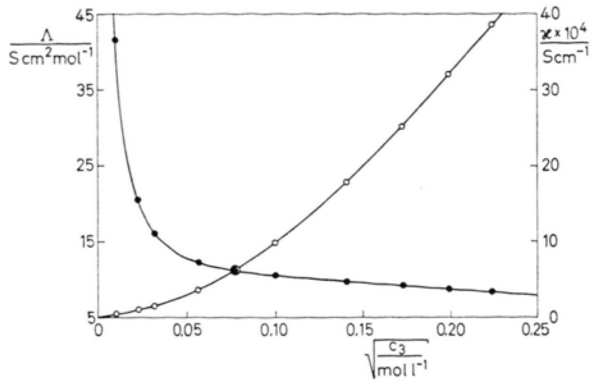

Fig. 3. Ternary system water + acetic acid + silver acetate at 25 °C: Conductivity $\varkappa$ and equivalent conductivity Λ as functions of the square root of the concentration c_3 of silver acetate for given ratio $c_3/c_2 = 0.1197$.

It is expedient to impose the condition [see Eq. (3)]

$$c_3/c_2 = C, \quad X_2 = 1/(1+C), \quad X_3 = C/(1+C), \tag{6}$$

where C is a constant. We then obtain from Eqs. (4) and (5) for infinite dilution ($c_2 \to 0$, $c_3 \to 0$, $\alpha_2 \to 1$, $\alpha_3 \to 1$):

$$\lim \Lambda = \lambda^0_{\mathrm{H^+}}/(1+C) + C\,\lambda^0_{\mathrm{Ag^+}}/(1+C) + \lambda^0_{\mathrm{Ac^-}} = \Lambda_2{}^0/(1+C) + C\,\Lambda_3{}^0/(1+C). \tag{7}$$

Here the $\lambda_i{}^0$ are the limiting values of the ionic conductivities (as given in tables for aqueous solutions at 25 °C) while $\Lambda_2{}^0$ and $\Lambda_3{}^0$ are the limiting values of Λ for the two binary systems water + acetic acid and water + silver acetate. We notice that in the ternary system, owing to the condition (6), the transition $c_2 \to 0$ (see Fig. 2) implies the transition $c_3 \to 0$ and vice versa (see Figure 3).

As far as the authors are aware, there are no previous experimental investigations on the electric conductivity of the ternary system considered here.