

Dilute Aqueous Solutions with Formate Ions: A Conductometric Study[†]

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Molar conductivities, Λ , of dilute aqueous solutions ($c = (\approx 3 \cdot 10^{-4}$ to $\approx 5 \cdot 10^{-3})$ mol·dm⁻³) of sodium formate, potassium formate, and formic acid in the temperature range $T = (278.15$ to $313.15)$ K are reported. The experimental data are examined by applying the Quint–Viillard conductivity equations and the Debye–Hückel equations for activity coefficients. Limiting conductivities of formate anion in the investigated temperature range were obtained from the data for salts, and then the dissociation constants for formic acid were estimated. Results were compared with the available literature data.

Introduction

Formic acid (methanoic acid) is the simplest carboxylic acid. It belongs to one of the basic organic chemicals, widely used in pesticide, leather, textile, dyeing, pharmaceutical, and rubber industries. This acid is also biologically important: it appears in fruits, vegetables, leaves, and roots of diverse plants and also in the secretions of numerous insects. It seems that formic acid inhibits or prevents mold growth, and therefore it is applied in silage and grain preservation. It helps, for instance, to keep certain foods fresh and free of salmonellae.¹ Currently researchers are working on making formic acid a source of energy for mobile phones and other portable electronic products equipped with microfuel cells.²

Despite its broad applications, the systematic investigations on the properties of formic acid aqueous solutions are rather scarce. Recently, the dissociation constant of formic acid in aqueous sodium chloride and potassium chloride solutions at 298.15 K has been determined.³ Surprisingly, there are no systematic studies of the transport properties of formic acid and its salts in the literature. There are some published data by Ostwald in 1889⁴ and Auerbach and Zeglin in 1922.⁵ Saxton and Darken reported later (1940) data on the electrical conductivity of formic acid and sodium formate,⁶ and Lobo collected the conductivity data on formic acid at different temperatures but at higher concentrations.⁷ However, nothing is known about the temperature dependence of transport properties of the formate ion in aqueous solutions.

In this work, we report precise measurements of molar conductivity, Λ , of dilute solutions of formic acid (HCOOH) and its sodium (HCOONa) and potassium salts (HCOOK) at temperatures $T = (278.15$ to $313.15)$ K in the concentration range $c = (\approx 3 \cdot 10^{-4}$ to $\approx 5 \cdot 10^{-3})$ mol·dm⁻³. From determined conductivities, the limiting molar conductivities of the formate anion and the dissociation constants of formic acid were derived as a function of temperature and compared with the literature values at 298.15 K.

In the optimization procedure, the law of mass action (activities were calculated using the Debye–Hückel equation

for activity coefficients) and the Quint–Viillard conductivity equation for formates and formic acid were applied to give a reliable set of derived parameters.

Experimental Section

Materials. Formic acid (HCOOH, > 98 %, Merck), sodium formate (HCOONa, puriss p. a., ≥ 99.0 %, Fluka), and potassium formate (HCOOK, ≥ 99.0 %, Sigma Aldrich) were used. Salts were dried for 48 h in vacuum at ≈ 390 K and stored in N₂ atmosphere. Demineralized water was distilled two times in a quartz bidistillation apparatus (Destamat Bi 18E, Heraeus). The final product with specific conductance $< 6 \cdot 10^{-7}$ Ω^{-1} cm⁻¹ was distilled into a flask permitting storage and transfer of water into the measuring cell under an atmosphere of nitrogen. Stock solutions were prepared by mass from formate salt or formic acid and water. All solutions were stored under nitrogen at room temperature. Concentration of the formic acid's stock solutions was checked by pH titration with standard sodium hydroxide solution (0.1 mol·dm⁻³ NaOH, Merck Titrisol).

Conductivity Measurements. The conductivities of the solutions were determined with the help of a three-electrode measuring cell, described elsewhere.⁸ The cell was calibrated with dilute potassium chloride solutions⁹ and immersed in the high-precision thermostat described previously.¹⁰ The temperature dependence of the cell constant was taken into account.⁹ The water bath can be set to each temperature using a temperature program with a reproducibility of 0.005 K. The temperature in the precision thermostat bath was additionally checked with a calibrated Pt100 resistance thermometer (MPMI 1004/300 Merz) in connection with a Multimeter HP 3458 A. The resistance measurements of the solutions in the cell were performed using a precision LCR Meter Agilent 4284 A.

At the beginning of every measuring cycle, the cell was filled with a known mass of water (≈ 660 g). After measurement of water conductivity at all temperatures of the temperature program, the stepwise concentration was carried out by successive additions of known masses of stock solution with a gastight syringe. After every addition, the temperature program was run by the computer, and all measured data (frequency dependent resistance, temperature) were stored and partially shown on display to track the measuring process. A home-developed software package was used for temperature control and acquisition of conductivity data. The measuring procedure,

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Table 1. Densities of Stock and Final Solutions in the Conductivity Cell of the Investigated Systems at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	$\rho/\text{kg}\cdot\text{dm}^{-3}$
Formic Acid (HCOOH)	
0	0.997048 ¹²
0.0048979	0.997113
0.12907	0.998530
Na Formate (HCOONa)	
0	0.997048 ¹²
0.0055911	0.997307
0.12223	1.002231
K Formate (HCOOK)	
0	0.997048 ¹²
0.0058309	0.997346
0.12191	1.002906

Table 2. Densities, d_0 , Viscosities, η , Relative Permittivity, ϵ , of Pure Water, and Limiting Ionic Conductivities, λ^0 , in Water at Temperatures from $T = (278.15 \text{ to } 313.15) \text{ K}$

T	d_0^{12}	$10^3\cdot\eta^{13}$	ϵ^{14}	$\lambda^0(\text{Na}^+)^{15}$	$\lambda^0(\text{K}^+)^{15}$	$\lambda^0(\text{H}^+)^{16}$
K	$\text{kg}\cdot\text{dm}^{-3}$	$\text{Pa}\cdot\text{s}$		$\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$
278.15	0.999967	1.5192	85.897	30.30	46.72	250.02
283.15	0.999702	1.3069	83.945	34.88	53.03	275.55
288.15	0.999102	1.1382	82.039	39.72	59.61	300.74
293.15	0.998206	1.0020	80.176	44.81	66.44	325.52
298.15	0.997048	0.8903	78.358	50.15	73.50	349.85
303.15	0.995651	0.7975	76.581	55.72	80.76	373.66
308.15	0.994036	0.7195	74.846	61.53	88.20	396.90
313.15	0.992219	0.6531	73.151	67.34	95.85	419.15

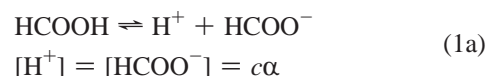
including corrections and extrapolation of the sample conductivity, κ , to infinite frequency, has been previously described.¹⁰

The densities, d , of the stock solutions and the final solutions in the conductivity cell, collected in Table 1, were determined by the method of Kratky et al.¹¹ using a Paar densimeter (DMA 60, DMA 601 HT) at $(298.15 \pm 0.01) \text{ K}$ combined with a precision thermostat. A linear change of d with increasing salt content for diluted solutions was assumed, $d = d_0 + b\cdot m$, where d_0 is the density of water, listed in Table 2 together with other known properties.^{12–15} From these data, the density gradients b for all examined electrolytes were determined. As usual, they

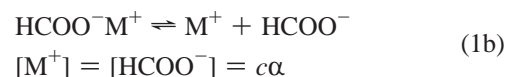
are considered to be independent of temperature and are quoted in corresponding Tables 3, 4, and 7 together with molar conductivities, $\Lambda = \kappa/c$, of all investigated systems. Molar conductivities are given as a function of electrolyte molality, m , which relates to the corresponding (temperature-dependent) molar concentration, c , via $c = m\cdot d/(1 + M_2\cdot m)$, where M_2 is the molar mass of the solute and d is the density of solution. The estimated uncertainty of d is within $0.005 \text{ kg}\cdot\text{m}^{-3}$. Considering the sources of error (calibration, measurements, impurities), the specific conductivities are estimated to be accurate to within 0.2 %.

Results and Discussion

Dissociation Equilibria and Conductivity Equations. The dissolution of formic acid HCOOH in terms of the dissociation reaction is governed by the following equations



where α denotes dissociation degree. If the ion pair–free ion equilibria are assumed in the case of formate salts then



where M^+ denotes Na^+ or K^+ . Material balance as expressed for formic acid and its salts is

$$c = [\text{H}^+] + [\text{HCOOH}] \quad (2a)$$

$$c = [\text{M}^+] + [\text{HCOO}^-\text{M}^+] \quad (2b)$$

and the mass-action equations representing the dissociation equilibrium can be written for acid as

$$K = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} Y = \frac{c^2\alpha^2}{c(1-\alpha)} Y \quad (3a)$$

and similarly for salts

Table 3. Experimental and Calculated Molar Conductivities, Λ , as a Function of Sodium Formate Molality, m , and Density Gradient, b , for HCOONa in Water

$10^3\cdot m$	T/K															
	$b = 0.0423 \text{ kg}^2\cdot\text{dm}^{-3}\cdot\text{mol}^{-1}$															
	$\Lambda/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$															
$\text{mol}\cdot\text{kg}^{-1}$	278.15		283.15		288.15		293.15		298.15		303.15		308.15		313.15	
	Λ_{exp}	Λ_{calc}	Λ_{exp}	Λ_{calc}	Λ_{exp}	Λ_{calc}	Λ_{exp}	Λ_{calc}	Λ_{exp}	Λ_{calc}	Λ_{exp}	Λ_{calc}	Λ_{exp}	Λ_{calc}	Λ_{exp}	Λ_{calc}
0.28733	62.600	62.45	71.91	71.73	81.67	81.58	91.85	91.84	102.47	102.52	113.43	113.55	124.71	124.86	135.76	135.75
0.38414	62.15	62.21	71.42	71.48	81.30	81.31	91.57	91.54	102.24	102.19	113.31	113.20	124.58	124.51	135.57	135.45
0.52467	61.87	61.89	71.11	71.16	80.93	80.95	91.18	91.15	101.82	101.77	112.84	112.75	124.27	124.06	135.08	135.08
0.56819	61.78	61.80	71.06	71.07	80.83	80.84	91.03	91.03	101.66	101.64	112.58	112.62	123.79	123.93	134.81	134.98
0.66082	61.58	61.61	70.81	70.88	80.58	80.63	90.78	90.80	101.39	101.39	112.40	112.36	123.73	123.66	134.67	134.77
0.82009	61.34	61.31	70.53	70.57	80.27	80.28	90.42	90.43	100.98	100.99	111.95	111.94	123.37	123.24	134.53	134.44
0.86292	61.07	61.23	70.49	70.48	80.19	80.19	90.31	90.33	100.88	100.89	111.83	111.83	123.06	123.13	134.42	134.36
0.95810	60.95	61.05	70.21	70.31	79.88	79.99	90.00	90.12	100.51	100.66	111.45	111.59	122.78	122.90	134.12	134.19
1.1194	60.88	60.77	70.02	70.03	79.65	79.68	89.75	89.79	100.25	100.30	111.15	111.21	122.48	122.53	134.01	133.91
1.1878	60.75	60.66	70.00	69.91	79.64	79.55	89.73	89.65	100.24	100.15	111.13	111.06	122.36	122.37	133.80	133.80
1.2569	60.54	60.54	69.86	69.80	79.48	79.42	89.57	89.51	100.06	100.01	110.96	110.91	122.28	122.22	133.65	133.69
1.5483	60.43		69.74		79.34		89.38		99.88		110.73		121.87		133.19	
1.9212	60.45		69.53		79.12		89.14		99.62		110.50		121.59		132.66	
2.3913	60.33		69.39		78.96		88.98		99.43		110.26		121.35		132.55	
3.0240	60.25		69.23		78.76		88.74		99.17		109.96		120.98		132.03	
3.7441	60.01		69.01		78.52		88.27		98.83		109.58		120.54		131.50	
4.5668	59.80		68.77		78.23		88.11		98.45		109.16		120.20		131.32	
5.5911	59.49		68.41		77.83		87.67		97.94		108.61		119.60		130.64	
	$\sigma(\Lambda)/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$															
	0.09		0.08		0.06		0.06		0.07		0.08		0.13		0.09	

$$K(\text{HCOO}^-\text{M}^+) = \frac{[\text{M}^+][\text{HCOO}^-]}{[\text{HCOO}^-\text{M}^+]} Y = \frac{c^2 \alpha^2}{c(1-\alpha)} Y \quad (3b)$$

$$\Lambda = \sum_{j=1}^n \frac{|z_j| c_j \lambda_j}{c} \quad (7)$$

where Y is the quotient of the activity coefficients, y_j , of corresponding species

$$Y = \frac{y_{\text{H}^+} y_{\text{HCOO}^-}}{y_{\text{HCOOH}}} \quad (4a)$$

$$Y = \frac{y_{\text{M}^+} y_{\text{HCOO}^-}}{y_{\text{HCOO}^-\text{M}^+}} \quad (4b)$$

The ionic activity coefficients of 1:1 electrolytes in dilute solution, y_j , can be approximated by the Debye–Hückel equation

$$\log[y_j(T)] = -\frac{z_j^2 A(T) \sqrt{I}}{1 + a_j B(T) \sqrt{I}}; I = \alpha \cdot c \quad (5)$$

$$A(T) = \frac{1.8246 \cdot 10^6}{[\varepsilon(T)T]^{3/2}}; B(T) = \frac{50.29 \cdot 10^8}{[\varepsilon(T)T]^{1/2}}$$

where $\varepsilon(T)$ is the relative permittivity of water; a_j is the ion distance parameter; and I denotes the ionic strength of the solution. In agreement with a large number of successful conductivity studies on aqueous solutions of monobasic acids,^{16,17} the site–site parameters of Kielland¹⁸ and Harris¹⁹ were chosen as the distance parameters a_j for the Debye–Hückel activity coefficients (eq 5) and consequently also for the conductivity equations and the thermodynamic functions in the chemical model to ensure compatibility. The temperature-independent site–site parameters were $a(\text{H}^+) = 0.9$ nm, $a(\text{HCOO}^-) = 0.5$ nm, $a(\text{Na}^+) = 0.4$ nm, and $a(\text{K}^+) = 0.35$ nm.

Dissociation degree α used in eqs 3a and 3b is evaluated in an iterative process applying the following quadratic equation¹⁶

$$\alpha = \frac{1}{2} \left[-\frac{K}{cY_1} + \sqrt{\left(\frac{K}{cY_1}\right)^2 + \frac{4K}{cY_1}} \right] \quad (6)$$

Quint–Viallard conductivity equations of dilute electrolyte solutions express molar electrolyte conductivity $\Lambda(c)$ as a function of the ionic conductivities λ_j of its constituting ions j of valency z_j at concentration c_j

$$\lambda_j = \lambda_j^0 - S_j \sqrt{I} + E_j I \ln I + J_{1j} I - J_{2j} I^{3/2}; I = \alpha c \quad (8)$$

where λ_j^0 is the limiting conductivity of an ion j and S_j , E_j , J_{1j} , and J_{2j} are ionic coefficients. Equation 8 represents ionic conductivity as a function of truncated series expansions of electrophoretic and relaxation effect with coefficients E_j , J_{1j} , and J_{2j} which depend on characteristic parameters and the boundary conditions underlying the specific molecular model.²⁰ The expressions of the Quint–Viallard equations are given in the literature.^{21–23} In the case of simple 1:1 salts or acid, we have $|z_+| = |z_-| = 1$; $c_+ = c_- = c$; and eq 7 reduces to

$$\Lambda = \alpha[\lambda(\text{M}^+) + \lambda(\text{HCOO}^-)] \quad (9)$$

$$\text{M}^+ = \text{H}^+, \text{Na}^+, \text{K}^+$$

Finally, the limiting molar conductivities Λ^0 according to Kohlrausch's law of independent migration of ions are

$$\Lambda^0 = \lambda^0(\text{M}^+) + \lambda^0(\text{HCOO}^-) \quad (10)$$

Thus, the proposed molecular model for the conductivity of formic acid and its salts in water includes the evaluation of the concentrations of all species present in solution (from eqs 1a to 6) and the use of Quint–Viallard conductivity equations (eq 9). The representation of the experimental conductivity–concentration data set (Λ , c) can formally be expressed in the form: $\Lambda = f[c; K, \lambda^0(\text{HCOO}^-), a_j]$. At a given temperature T , the physical properties of pure water^{12–14} and the limiting ionic conductivities $\lambda^0(\text{H}^+)$, $\lambda^0(\text{Na}^+)$, and $\lambda^0(\text{K}^+)$ are known from the literature¹⁵ (Table 2), and the distances of closest approach in the Quint–Viallard conductivity equations can be taken as the average value of the ion size parameters in the ion pairs. Therefore, the optimization problem requires the determination of two unknown parameters, dissociation constant K and limiting molar conductivity of formate anion $\lambda^0(\text{HCOO}^-)$.

The iterative process starts with the assumed dissociation constant K , and the values of α , y_j , and I for each concentration c were calculated and introduced into the computer program with the Quint–Viallard conductivity equations to obtain the limiting conductivity of the HCOO^- anion. The calculations were repeated with new value of K until the

Table 4. Experimental and Calculated Molar Conductivities, Λ , as a Function of Potassium Formate Molality, m , and Density Gradient, b , for HCOOK in Water

10 ³ ·m mol·kg ⁻¹	T/K															
	$b = 0.0480 \text{ kg}^2 \cdot \text{dm}^{-3} \cdot \text{mol}^{-1}$															
	$\Lambda/\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$															
	278.15		283.15		288.15		293.15		298.15		303.15		308.15		313.15	
	Λ_{exp}	Λ_{calc}	Λ_{exp}	Λ_{calc}	Λ_{exp}	Λ_{calc}	Λ_{exp}	Λ_{calc}	Λ_{exp}	Λ_{calc}	Λ_{exp}	Λ_{calc}	Λ_{exp}	Λ_{calc}	Λ_{exp}	Λ_{calc}
0.34976	79.06	78.92	90.19	90.04	101.80	101.64	113.76	113.61	126.03	125.99	138.66	138.63	151.63	151.46	164.92	164.57
0.65989	78.26	78.41	89.31	89.46	100.83	100.99	112.75	112.89	125.14	125.21	137.69	137.81	150.23	150.63	163.17	163.66
1.0258	77.89	77.92	88.88	88.90	100.32	100.36	112.13	112.21	124.46	124.47	137.09	137.04	150.00	149.87	162.80	162.81
1.4120	77.52	77.47	88.44	88.39	99.84	99.78	111.70	111.59	123.92	123.80	136.51	136.34	149.44	149.19	162.23	162.07
1.7660	77.01	77.10	87.87	87.97	99.19	99.31	110.97	111.07	123.12	123.25	135.63	135.78	148.53	148.65	161.42	161.47
2.2175	76.74	76.67	87.55	87.47	98.86	98.75	110.55	110.47	122.65	122.61	135.15	135.13	148.00	148.03	160.82	160.79
2.8227	76.53		87.29		98.52		110.23		122.31		134.80		147.64		160.56	
3.4318	76.32		87.06		98.26		109.95		121.98		134.41		147.22		160.10	
4.0602	76.11		86.82		98.00		109.65		121.67		134.06		146.82		159.62	
4.8154	75.96		86.65		97.80		109.42		121.43		133.78		146.50		159.33	
5.8309	75.73		86.37		97.48		109.06		121.03		133.32		145.99		158.68	
	$\sigma(\Lambda)/\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$															
	0.11		0.12		0.13		0.13		0.09		0.12		0.24		0.28	

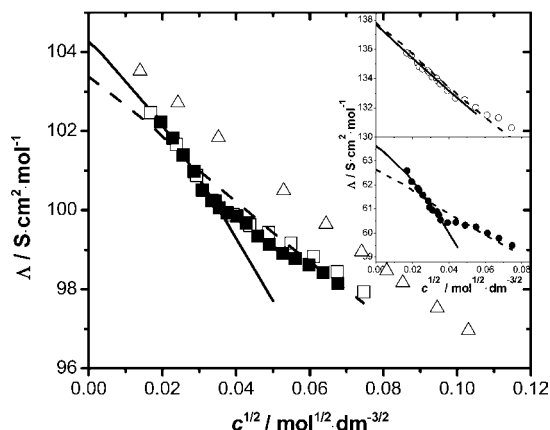


Figure 1. Molar conductivity, Λ , of sodium formate at 298.15 K: \square , first and \blacksquare , second run in this study, respectively; Δ , ref 6. Solid line represents the best fit of the QV model (eqs 1a to 9) for the first eleven points ($c < 1.5 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) and the dashed line the best fit of the QV model including hydrolysis (eqs 17 to 31) for the entire concentration range. Inset: experimental and calculated molar conductivities: \bullet , at 278.15 K and \circ , at 313.15 K.

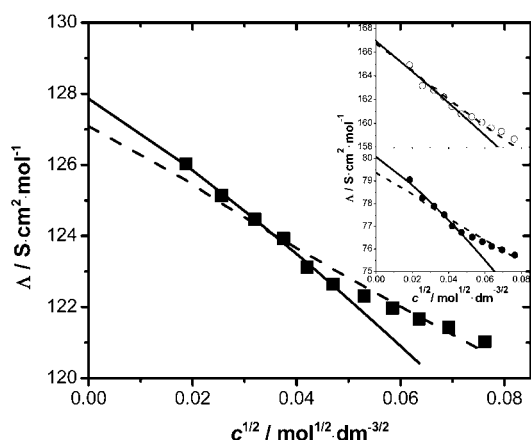


Figure 2. Molar conductivity, Λ , of potassium formate at 298.15 K. Solid line represents the best fit of the QV model (eqs 1a to 9) for the first six points ($c < 2.2 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) and the dashed line the best fit of the QV model including hydrolysis (eqs 17 to 31) for the entire concentration range. Inset: experimental and calculated molar conductivities: \bullet , at 278.15 K and \circ , at 313.15 K.

satisfactory agreement between the measured and calculated conductivities $\Lambda(c)$ was reached. The degree of agreement of the obtained fit is expressed by the mean value of standard deviations

$$\sigma(\Lambda) = \sqrt{\frac{\sum_{j=1}^n (\Lambda_{j,\text{exp}} - \Lambda_{j,\text{calc}})^2}{N - 1}} \quad (11)$$

where $\Lambda_{j,\text{exp}}$ is the experimental value of molar conductivity; $\Lambda_{j,\text{calc}}$ is the calculated value; and N is the number of data points. The error was estimated as the square roots of diagonal elements of the variance-covariance matrix.

Electrical Conductivities of Sodium Formate and Potassium Formate. Experimental molar conductivities of sodium formate and potassium formate show two different regions which are concentration and temperature dependent; see Figure 1 for HCOONa and Figure 2 for HCOOK. For concentrations lower than $1.5 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ in the case of HCOONa and $2.2 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ in the case of HCOOK, formate salts behave like strong 1:1 electrolytes, but at higher concentration an

Table 5. Temperature Dependence of the Limiting Molar Ion Conductivities, $\lambda^0(\text{HCOO}^-)$, as Derived from HCOONa and HCOOK Aqueous Solution Conductivities and the Corresponding Walden Products $\eta \cdot \lambda_{\text{av}}^0$

T/K	$\lambda^0(\text{HCOO}^-)/\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$			$10^6 \cdot \eta \cdot \lambda_{\text{av}}^0 / \text{S} \cdot \text{kg} \cdot \text{m} \cdot \text{s}^{-1} \cdot \text{mol}^{-1}$
	from HCOONa	from HCOOK	average	
278.15	33.32 ± 0.09	33.35 ± 0.11	33.33 ± 0.10	5.064
283.15	38.11 ± 0.07	38.35 ± 0.12	38.23 ± 0.10	4.996
288.15	43.29 ± 0.06	43.54 ± 0.13	43.42 ± 0.10	4.942
293.15	48.61 ± 0.05	48.86 ± 0.13	48.73 ± 0.09	4.883
298.15	54.11 ± 0.06	54.35 ± 0.09	54.23 ± 0.07	4.828
303.15	59.73 ± 0.07	59.89 ± 0.12	59.81 ± 0.10	4.770
308.15	65.34 ± 0.12	65.41 ± 0.25	65.37 ± 0.19	4.704
313.15	70.35 ± 0.08	71.09 ± 0.29	70.72 ± 0.19	4.619

unexpected behavior is evident for both systems. Therefore, the measurement for HCOONa was repeated to check the experiment and to obtain more data in the extremely diluted region. In Figure 1 the data for both experimental series are presented, and they are in good agreement. It can be assumed that at higher concentrations some additional processes influence the deviation.

First we focus our attention on the extremely diluted concentration range where both salts can be regarded as typical 1:1 electrolytes. The QV set of equations (eqs 1a to 9) was applied to fit the model to the experimental conductivities. The results of experimental Λ_{exp} and calculated Λ_{calc} molar conductivities of HCOONa and HCOOK salts, together with the standard deviations $\sigma(\Lambda)$, are presented in Tables 3 and 4, respectively. As can be observed, there is a reasonable agreement between the experimental and calculated conductivities over the investigated concentration region and at all temperatures. The quantity of interest, limiting molar conductivity of HCOO^- as a function of temperature, together with Walden products are presented in Table 5. The values obtained from HCOONa agree with those calculated from HCOOK. The Walden product of the HCOO^- anion is temperature dependent. The obtained constants for the dissociation equilibrium (eq 3b) at 298.15 K are $K(\text{HCOO}^- \text{Na}^+) = (0.080 \pm 0.005) \text{ mol} \cdot \text{dm}^{-3}$ and $K(\text{HCOO}^- \text{K}^+) = (0.19 \pm 0.02) \text{ mol} \cdot \text{dm}^{-3}$ assuming that the ions are in contact.

There are a lack of experimental conductivity data on formate salts. The only investigation was performed by Saxton and Darken⁶ at 298.15 K. Their data are presented in Figure 1 together with results of this work, and the differences between the measured molar conductivities are evident. This discrepancy could come from the sample preparation: in our work pure salt was applied, whereas Saxton and Darken prepared the salt solutions by adding the calculated quantity of pure sodium carbonate to the acid solution. Nevertheless, the reported limiting molar conductivity of HCOO^- ($\lambda^0(\text{HCOO}^-) = 54.54 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) and our value of $\lambda^0(\text{HCOO}^-) = (54.23 \pm 0.07) \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ are very close. The literature data were reanalyzed, and the obtained value for $\lambda^0(\text{HCOO}^-)$ is the same as reported by Apelblat et al. for the same approach applied at the same source of data ($\lambda^0(\text{HCOO}^-) = 54.64 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$).¹⁶

If the Eyring approach is applied to the temperature dependence of the limiting conductivities, then

$$\left(\frac{\partial \ln[\lambda^0(T)d_0^{2/3}(T)]}{\partial T} \right)_P = \frac{\Delta H_{\lambda}^{\ddagger}}{RT^2} \quad (12)$$

where $\Delta H_{\lambda}^{\ddagger}$ is the partial molar enthalpy associated with the ion movement. When $\Delta H_{\lambda}^{\ddagger}$ is independent of temperature, the integral form of eq 12 is

$$\ln[\lambda^0(T)d_0^{2/3}(T)] = -\frac{\Delta H_\lambda^\ddagger}{RT} + \text{const.} \quad (13)$$

Using densities of pure water d_0 from Table 2 and the average limiting conductivities from Table 5, we have

$$\ln[\lambda^0(T)d_0^{2/3}(T)] = 10.221 - \frac{1861.8}{(T/K)}; R^2 = 0.9967 \quad (14)$$

where $\Delta H_\lambda^\ddagger = 15.5 \text{ kJ}\cdot\text{mol}^{-1}$.

For concentrations larger than $1.5\cdot 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ (HCOONa) and $2.2\cdot 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ (HCOOK), experimental molar conductivities do not follow the behavior of strong 1:1 electrolytes. This concentration-dependent effect is shown in Figure 1 for HCOONa and Figure 2 for HCOOK. At lower temperatures the effect is very strong, whereas at higher temperatures it vanishes (see insets in Figures 1 and 2). Clearly, different equilibria are present in this concentration range.

To improve the agreement between calculated and experimental molar conductivities through the entire concentration range, the hydrolysis process²⁴ was introduced into the QV set of equations. The mathematical derivation for this hydrolysis process is presented in the Appendix. Formally, two parameters can be determined by the fitting procedure, dissociation constant of formic acid and limiting molar conductivity of HCOO^- . Actually, only $\lambda^0(\text{HCOO}^-)$ can be determined, whereas the dissociation constant of formic acid must be known. Results for HCOONa and HCOOK, with the hydrolysis process included, at 298.15 K are presented in Figures 1 and 2. The evaluated parameters for HCOOK are presented also in Table

Table 6. Fractions of Free Ions, α , and Hydrogen Ions, β , and Experimental and Calculated Molar Conductivities, Λ , for the Entire Concentration Range at 298.15 K for Potassium Formate (HCOOK) as Obtained with Included Hydrolysis Process

$10^3 \cdot c$ $\text{mol}\cdot\text{dm}^{-3}$	α	β	Λ_{exp} $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	Λ_{calc} $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$\Delta\Lambda$ $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$
0.3487	0.999630	0.000161	126.03	125.57	0.46
0.6579	0.999709	0.000068	125.14	124.91	0.23
1.023	0.999759	0.000037	124.46	124.35	0.11
1.408	0.999791	0.000024	123.92	123.87	0.05
1.761	0.999811	0.000017	123.12	123.49	-0.37
2.211	0.999830	0.000012	122.65	123.07	-0.42
2.814	0.999848	0.000009	122.31	122.58	-0.27
3.421	0.999862	0.000007	121.98	122.14	-0.16
4.047	0.999872	0.000005	121.67	121.73	-0.06
4.800	0.999882	0.000004	121.43	121.28	0.15
5.811	0.999893	0.000003	121.03	120.74	0.29

Table 7. Experimental and Calculated Molar Conductivities, Λ , as a Function of Formic Acid Molality, m , and Density Gradient, b , for HCOOH in Water

$10^3 \cdot m$ $\text{mol}\cdot\text{kg}^{-1}$	T/K															
	$b = 0.0114 \text{ kg}^2\cdot\text{dm}^{-3}\cdot\text{mol}^{-1}$															
	$\Lambda/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$															
	278.15		283.15		288.15		293.15		298.15		303.15		308.15		313.15	
	Λ_{exp}	Λ_{calc}	Λ_{exp}	Λ_{calc}	Λ_{exp}	Λ_{calc}	Λ_{exp}	Λ_{calc}	Λ_{exp}	Λ_{calc}	Λ_{exp}	Λ_{calc}	Λ_{exp}	Λ_{calc}	Λ_{exp}	Λ_{calc}
0.27088	148.98	145.99	164.78	162.12	180.092	177.99	194.68	193.36	208.43	208.16	221.37	222.23	233.48	235.19	242.47	246.42
0.56568	113.19	112.87	125.40	125.39	137.63	137.69	149.45	149.56	160.78	160.93	171.49	171.69	180.06	181.50	188.96	189.82
0.82981	97.05	97.47	108.02	108.29	118.76	118.92	129.15	129.17	139.09	138.96	148.52	148.21	157.28	156.60	164.04	163.67
1.0940	86.74	87.28	96.48	96.99	106.12	106.52	115.40	115.69	124.33	124.45	132.79	132.70	140.71	140.18	146.56	146.43
1.4421	77.35	77.92	86.18	86.59	94.84	95.10	103.23	103.28	111.29	111.09	118.94	118.44	125.95	125.08	132.17	130.61
1.8252	68.97	70.56	76.83	78.42	84.54	86.13	91.99	93.54	99.14	100.61	105.97	107.25	112.34	113.24	117.16	118.21
2.2220	63.65	64.87	70.94	72.09	78.10	79.18	85.03	85.99	91.71	92.48	98.07	98.58	104.04	104.07	109.33	108.61
2.6483	59.34	60.11	66.08	66.81	72.68	73.39	79.02	79.70	85.10	85.71	90.72	91.35	95.89	96.43	100.95	100.61
3.2077	54.77	55.27	61.08	61.43	67.28	67.47	73.28	73.27	79.06	78.80	84.50	83.98	89.36	88.63	93.91	92.46
3.9574	50.45	50.35	56.27	55.97	61.99	61.47	67.53	66.76	72.87	71.78	77.88	76.50	82.42	80.73	86.60	84.20
4.8979	46.33	45.76	51.68	50.86	56.95	55.87	62.06	60.67	66.99	65.24	71.67	69.52	75.98	73.35	79.88	76.50
	$\sigma(\Lambda)/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$															
	1.23		1.13		1.02		0.90		0.87		1.01		1.34		2.00	

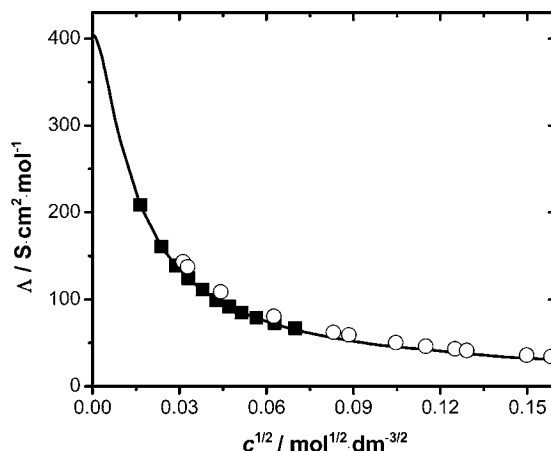


Figure 3. Molar conductivities, Λ , of formic acid at 298.15 K: ■, this study; ○, ref 6. Solid line represents the best fit of the Quint-Viallard model using eqs 1a to 9.

6. Evidently, in the case of HCOOK ion pairs, K^+ and HCOO^- contribute by far the most to the overall conductivity ($\alpha > 0.999$, eq 30). The other two terms in eq 30 come from introducing the hydrolysis process. Ion pairs K^+ and OH^- ($1 - \alpha$) and H^+ and OH^- ($\beta < 1.6\cdot 10^{-4}$) contribute a rather small part to overall conductivity. Limiting molar conductivity at 298.15 K was found to be $\lambda^0(\text{HCOO}^-) = (53.59 \pm 0.43) \text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ($\lambda^0(\text{HCOO}^-) = (53.23 \pm 0.31) \text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ from HCOONa), which is $0.64 \text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ smaller than that obtained from analysis of the linear part, where only concentrations of the salt smaller than $2.2\cdot 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ were taken into account. The results of fitting the data of HCOONa are not presented in the table due to the even higher deviations.

Electrical Conductivities of Formic Acid. The results of experimental Λ_{exp} and calculated Λ_{calc} molar conductivities of formic acid HCOOH, together with the standard deviations $\sigma(\Lambda)$, are presented in Table 7. The QV model was fitted to the experimental conductivities by applying eqs 1a to 9. In this case, only the dissociation constant of acid K (eq 3a) was set as variable. The $\lambda^0(\text{HCOO}^-)$ can not be determined accurately because of the long extrapolation to zero concentration. Therefore, the value for $\lambda^0(\text{HCOO}^-)$ was taken as an average value obtained from sodium and potassium salt for a given temperature. Agreement between measured and calculated molar conductivities is shown in Figure 3 together with the literature data.⁶ The obtained dissociation constant as a function of

Table 8. Dissociation Constant of HCOOH as a Function of Temperature

<i>T</i> /K	<i>K</i> ·10 ⁴ /mol·dm ⁻³
278.15	1.46 ± 0.15
283.15	1.47 ± 0.13
288.15	1.48 ± 0.10
293.15	1.47 ± 0.08
298.15	1.46 ± 0.08
303.15	1.44 ± 0.08
308.15	1.40 ± 0.10
313.15	1.35 ± 0.14

temperature is presented in Table 8. At 298.15 K, $K = (1.46 \pm 0.08) \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, and it differs considerably from QV analysis of the literature data⁶ performed by Apelblat et al.,^{16,25} $K = 1.84 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$. The dissociation constant is slightly temperature dependent. The average value in the temperature range between (278.15 and 313.15) K is $K_{\text{av}} = (1.44 \pm 0.11) \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$.

The standard thermodynamic functions of the dissociation process are defined by the equations

$$\begin{aligned} \Delta G^0 &= -RT \ln K \\ \Delta G^0 &= \Delta H^0 - T\Delta S^0 \\ \Delta S^0 &= -\left(\frac{\partial \Delta G^0}{\partial T}\right)_P \end{aligned} \quad (15)$$

The Gibbs free energy can be linearly correlated with T , $\Delta G^0(T)/\text{kJ} \cdot \text{mol}^{-1} = -1.5936 + 0.0789(T/\text{K})$, $R^2 = 0.9978$. At 298.15 K, $\Delta G^0 = 21.9 \text{ kJ} \cdot \text{mol}^{-1}$, $T\Delta S^0 = -23.5 \text{ kJ} \cdot \text{mol}^{-1}$, and $\Delta H^0 = -1.6 \text{ kJ} \cdot \text{mol}^{-1}$. It follows that the dissociation is only controlled by entropy because $\Delta G^0 \approx -T\Delta S^0$ and $\Delta H^0 \approx -0.1\Delta G^0$.

Conclusions

Molar conductivities, Λ , for dilute solutions of formic acid and its sodium and potassium salt in water were determined as a function of temperature. Whereas at formic acid aqueous solutions an expected behavior was found, the opposite is true for both investigated salts. Sodium and potassium salts show two regions with almost linear dependence of Λ on the square of concentration but with different slopes (Figures 1 and 2).

In this work, first the data in extremely diluted solutions ($c \leq 0.0015 \text{ mol} \cdot \text{dm}^{-3}$ for HCOONa and $c \leq 0.0022 \text{ mol} \cdot \text{dm}^{-3}$ for HCOOK) were analyzed with the Quint–Viallard set of conductivity equations, yielding the limiting values of molar conductivity, Λ^0 . From known limiting ionic conductivities for sodium and potassium ion, the limiting ionic conductivities of the formate ion were determined in the investigated temperature range. The values obtained from HCOONa agree with those calculated from HCOOK at all temperatures.

The unexpected behavior at concentrations higher than $0.0015 \text{ mol} \cdot \text{dm}^{-3}$ and $0.0022 \text{ mol} \cdot \text{dm}^{-3}$ for HCOONa and HCOOK, respectively, should be ascribed to an additional process in the solutions, which is important at higher concentrations. Here an attempt was made to include the hydrolysis in the treating of the conductivity data, where the deviation from the expected behavior is not significant. Small improvement of fitting at the experimental data was obtained, but unfortunately the estimated limiting molar conductivities differ significantly from those yielded from the experimental data of extremely diluted solutions. Therefore, the observed unusual behavior of conductivities in aqueous solutions at the moderate concentrations of formate salts still remains unexplained.

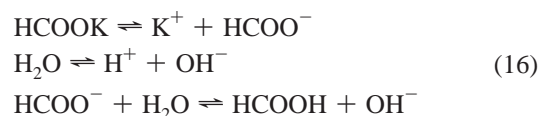
Using the limiting ionic conductivities of formate ion, the limiting molar conductivities of formic acid were calculated at all temperatures and used as an input parameter at evaluation of the dissociation constants of formic acid. The only possible comparison of K values based on the Quint–Viallard conductivity equation with those coming from the literature conductivities is at 298.15 K only. The determined value ($K = 1.46 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$) is considerably lower than that from the literature ($K = 1.84 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$), despite the fact that the experimental data are in both cases in good agreement. The dissociation constants derived here from conductivity measurements show only weak temperature dependence. In the temperature range between (278.15 and 313.15) K an average value $K_{\text{av}} = (1.44 \pm 0.11) \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ has been found.

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Appendix

The simplest version of hydrolysis which will be responsible for the deviation of potassium (the same for sodium) formate salt from the behavior of a strong 1:1 electrolyte includes the following set of reactions²⁴



The mass-action equations of the hydrolysis process are therefore

$$K = \frac{a_{\text{H}^+} a_{\text{HCOO}^-}}{a_{\text{HCOOH}}} = \frac{[\text{H}^+][\text{HCOO}^-]^{y_{\text{H}^+} y_{\text{HCOO}^-}}}{[\text{HCOOH}]^{y_{\text{HCOOH}}}} = \frac{[\text{H}^+][\text{HCOO}^-]^{Y_1}}{[\text{HCOOH}]^{Y_1}} \quad (17)$$

$$Y_1 = y_{\text{H}^+} y_{\text{HCOO}^-}; y_{\text{HCOOH}} = 1$$

and

$$\begin{aligned} K_w &= a_{\text{H}^+} a_{\text{OH}^-} = [\text{H}^+][\text{OH}^-]^{y_{\text{H}^+} y_{\text{OH}^-}} = [\text{H}^+][\text{OH}^-]^{Y_2} \\ Y_2 &= y_{\text{H}^+} y_{\text{OH}^-} \end{aligned} \quad (18)$$

Denoting

$$\begin{aligned} [\text{K}^+] &= c \\ [\text{HCOO}^-] &= c\alpha_{\text{HCOO}^-} = c\alpha \\ [\text{H}^+] &= c\alpha_{\text{H}^+} = c\beta \\ [\text{OH}^-] &= c\alpha_{\text{OH}^-} \\ [\text{HCOOH}] &= c\alpha_{\text{HCOOH}} \end{aligned} \quad (19)$$

the material and charge balance equations are

$$\begin{aligned} [\text{HCOOK}] &= [\text{HCOO}^-] + [\text{HCOOH}] \\ c &= c\alpha_{\text{HCOO}^-} + c\alpha_{\text{HCOOH}} = c\alpha + c\alpha_{\text{HCOOH}} \\ \alpha_{\text{HCOOH}} &= 1 - \alpha \\ [\text{K}^+] + [\text{H}^+] &= [\text{OH}^-] + [\text{HCOO}^-] \\ c + c\alpha_{\text{H}^+} &= c\alpha_{\text{OH}^-} + c\alpha_{\text{HCOO}^-} \\ 1 + \beta &= \alpha_{\text{OH}^-} + \alpha \\ \alpha_{\text{OH}^-} &= 1 + \beta - \alpha \end{aligned} \quad (20)$$

In terms of the concentration fractions α and β , the mass-action equations are by

$$K = \frac{[H^+][HCOO^-]}{[HCOOH]} Y_1 = \frac{c\alpha\beta}{1-\alpha} Y_1 \quad (21)$$

$$K_w = [H^+][OH^-] Y_2 = c^2\beta(1 + \beta - \alpha) Y_2 \quad (22)$$

The ionic strength I is equal to

$$I = \frac{1}{2} \sum_i z_i^2 c_i = \frac{1}{2} [c_{K^+} \cdot 1^2 + c_{H^+} \cdot 1^2 + c_{OH^-} \cdot 1^2 + c_{HCOO^-} \cdot 1^2]$$

$$I = \frac{1}{2} [c + c\beta + c(1 + \beta - \alpha) + c\alpha] = c(1 + \beta) \quad (23)$$

Using eq 22, we have from the Taylor series

$$\alpha = \frac{K}{K + c\beta Y_1} = \frac{1}{1 + \frac{c\beta Y_1}{K}} = 1 - \frac{c\beta Y_1}{K} + \left(\frac{c\beta Y_1}{K}\right)^2 - \dots \quad (24)$$

Since $c\beta Y_1/K \ll 1$, the linear term is enough in the expansion, and therefore introducing α from eq 24 into eq 22 we obtain

$$K_w = c^2\beta \left(1 + \beta - 1 + \frac{c\beta Y_1}{K}\right) Y_2 \quad (25)$$

and finally the fraction of hydrogen ions as

$$\beta = \sqrt{\frac{KK_w}{c^2 Y_2 (K + c Y_1)}} \quad (26)$$

Thus, in terms of concentrations, we have

$$[H^+] = c\beta = \sqrt{\frac{KK_w}{(K + cF_1)Y_2}}$$

$$[HCOO^-] = c\alpha = \frac{Kc}{K + c\beta Y_1} \quad (27)$$

$$[OH^-] = c(1 + \beta - \alpha)$$

$$[HCOOH] = c(1 - \alpha)$$

The ionic contributions to the molar conductivity Λ

$$\Lambda = \frac{1000\kappa}{c} = \sum_i \frac{|z_i|c_i}{c} \lambda_i = \sum_i \alpha_i \lambda_i \quad (28)$$

$$\Lambda = \lambda(K^+) + \beta\lambda(H^+) + \alpha\lambda(HCOO^-) + (1 + \beta - \alpha)\lambda(OH^-)$$

where the individual ionic contributions have the form

$$\lambda_i = \lambda_i^0 + S_i \sqrt{c(1 + \beta)} + E_i c(1 + \beta) \ln[c(1 + \beta)] + J_{1i} c(1 + \beta) - J_{2i} [c(1 + \beta)]^{3/2} \quad (29)$$

Equation 28 can be also written in the form of three contributions

$$\Lambda = \alpha\Lambda_1 + (1 - \alpha)\Lambda_2 + \beta\Lambda_3 \quad (30)$$

where

$$\Lambda_1 = [\lambda(K^+) + \lambda(HCOO^-)]$$

$$\Lambda_2 = [\lambda(K^+) + \lambda(OH^-)] \quad (31)$$

$$\Lambda_3 = [\lambda(H^+) + \lambda(OH^-)]$$

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