Electric Conductivity in Molten Binaries of Alkali Formates and Acetates

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The conductivity, κ, and the apparent activation energy, E_κ, in molten pure HCOONa, HCOOK, and HCOORb and in the molten binary mixtures (Na,K)HCOO, (Na,Rb)HCOO, (K,Rb)HCOO, and ($HCOO,CH_3COO$)K, are measured, and an empirical equation connecting the conductivity, κ, to the composition, x, and to the temperature is given. Deviations from the additivity are shown.

Some properties of molten mixtures containing sodium and potassium acetates and formates were discussed previously (*1, 3, 4*). The present paper deals with the conductivity, κ, and the activation energy, E_κ, of the molten pure HCOONa, HCOOK, and HCOORb and of the molten binary mixtures (Na,K)HCOO, (Na,Rb)HCOO, (K,Rb)HCOO, and ($HCOO,CH_3COO$)K at various temperatures.

Experimental

Chemicals. C. Erba RP sodium and rubidium formate, potassium formate and acetate (mp 531, 443, 442, and 579K, respectively), carefully dried under vacuum at 120°C, were used.

Measurements of temperature and conductivity. The apparatus, procedure, and assessment of probable errors for these measurements were described elsewhere (3).

Results

The conductivity dependence on the composition, x, at fixed temperatures for the four binary systems is shown in Figure 1. In Figure 2 are reported the $\Delta\kappa (\Delta\kappa = \kappa_{\text{calc}} - \kappa_{\text{exp}})$ vs. x, at fixed temperatures.

The $\Delta\kappa$ deviations are not regular in the mixtures examined. In fact, these deviations for the (Na,K)HCOO mixtures present an "S"-shaped behavior. In the (Na,Rb)HCOO and ($HCOO,CH_3COO$)K mixtures, they are always negative in respect to the additivity and increase with the temperature; the (K,Rb)HCOO mixtures present the highest negative deviations at lowest temperatures. Generally, the larger the differences in the sizes of the cations (or anions) in the melt mixtures, the greater are the deviations from the additivity (2).

The dependence of the conductivity κ on the temperature Kelvins at fixed compositions is always represented by the linear equation:

$$\kappa = -a + bT \qquad (1)$$

The values of the parameters are summarized in Table I. The deviations between the κ experimental and the κ calculated by Equation 1 are in each case less than 1%. By the methods reported in the previous note (3), for the four systems, it is possible to obtain an equation of the form:

$$\kappa = -(a_0 + b_0x + c_0x^2) + (a_1 + b_1x + c_1x^2)T \qquad (2)$$

connecting the conductivity to the composition and the temperature. The parameter's values of Equation 2 are reported in Table II.

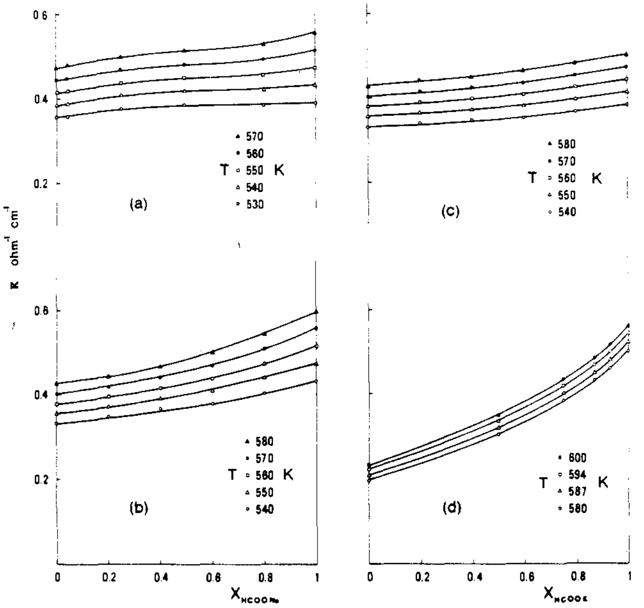

Figure 1. Conductivity dependence with HCOONa or HCOOK molar fraction at fixed temperatures for systems: (a) (Na,K)HCOO; (b) (Na,Rb)HCOO; (c) (K,Rb)HCOO; (d) ($HCOO,CH_3COO$)K

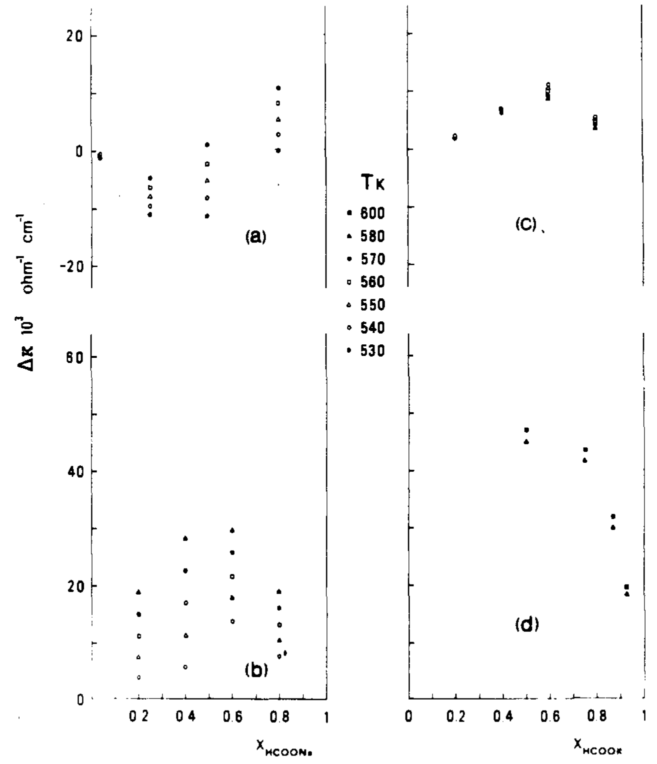

Figure 2. $\Delta\kappa$ (i.e., $\kappa_{\text{theor}} - \kappa_{\text{exp}}$) dependence with HCOOK or HCOONa molar fraction at fixed temperatures for systems: (a) (Na,K)HCOO; (b) (Na,Rb)HCOO; (c) (K,Rb)HCOO; (d) ($HCOO,CH_3COO$)K

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Table I. Parameter Values of Equation 1

System	Composition	a	$b \cdot 10^3$
(Na,K)HCOO	x_{HCOONa} 1.000	1.7970	4.127
	0.800	1.5345	3.619
	0.495	1.3222	3.220
	0.250	1.2534	3.074
	0.043	1.2361	3.008
	0.000	1.1995	2.935
(Na,Rb)HCOO	x_{HCOONa} 1.000	1.7970	4.127
	0.800	1.4814	3.491
	0.600	1.2567	3.026
	0.400	0.9896	2.509
	0.200	0.9182	2.343
	0.000	0.9476	2.367
(K,Rb)HCOO	x_{HCOOK} 1.000	1.1995	2.935
	0.800	1.1814	2.871
	0.600	1.1440	2.771
	0.400	1.0471	2.580
	0.200	1.0064	2.492
	0.000	0.9476	2.367
(HCOO,$CH_3 \cdot$COO)K	x_{HCOOK} 1.000	1.1995	2.935
	0.930	1.1594	2.797
	0.870	1.1303	2.695
	0.750	1.1018	2.562
	0.500	1.0127	2.270
	0.000	0.8506	1.803

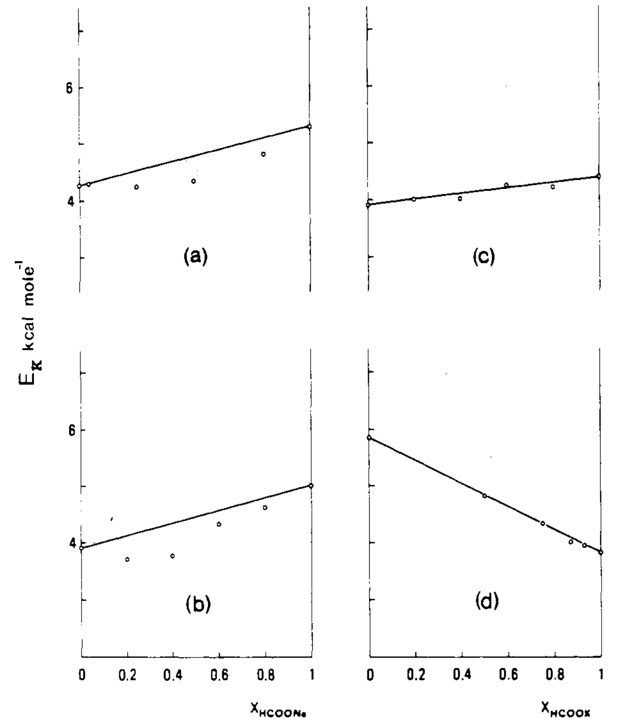

Figure 3. Activation energy as function of HCOONa of HCOOK molar fraction for systems: (a) (Na,K)HCOO; (b) (Na,Rb)HCOO; (c) (K,Rb)HCOO; (d) (HCOO,CH_3COO)K

Table II. Parameter Values of Equation 2

	(Na,K)HCOO	(Na,Rb)HCOO	(K,Rb)HCOO	(HCOO,-$CH_3 \cdot$COO)K
a_0	1.7822	0.9278	0.9404	0.8514
b_0	−1.2592	−0.1577	0.3655	0.2947
c_0	0.7015	1.0439	−0.09673	0.04440
a_1	0.004094	0.002333	0.002356	0.001806
b_1	−0.002349	−0.0001823	0.0007101	0.0007020
c_1	0.001238	0.002008	−0.0001147	0.0004030

The deviations between the κ experimental and the κ calculated by Equation 2 are in each case less than 1%. The apparent activation energy E_κ was determined by the Arrhenius equation, by plotting log κ vs. $1/T$ for the pure salts and for the different mixtures. The plot of the E_κ values vs. the composition and the comparison with the additive behavior of the mixtures for each system are shown in Figure 3.

Discussion

In the systems (Na,K)CH_3COO (*3*), (Na,K)HCOO, (K,Rb)HCOO, (Na,Rb)HCOO, and (HCOO,CH_3COO)K, the apparent activation energy E_κ shows a large negative deviation with respect to additivity, when the Na^+ ion is present. In the other cases, the behavior is more or less additive. The small sizes, by consequence higher charge density, of the Na^+ ion as to K^+ and Rb^+ ions, are able to explain this fact.

On the other hand, in the (Na,K)HCOO mixtures, the positive deviation of the κ_{exp} causes a negative deviation of the E_κ, as could be expected. For the other systems, while the κ_{exp} are smaller than κ_{calc}, the E_κ values show a negative deviation in the (Na,Rb)HCOO and (K,Na)-CH_3COO mixtures, or an additive behavior in the (K,Rb)HCOO and (HCOO,CH_3COO)K mixtures.

Probably, the difference in the sizes of ions in the melts is the reason for this behavior, and only the continuation of this research will be able to strengthen this conjecture.

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