Electric Conductivity and Density of Sodium-Rubidium and Sodium-Cesium Acetate Molten Mixtures

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The electric conductivities, densities and activation energies of RbC$_2$H$_3$O$_2$ and CsC$_2$H$_3$O$_2$ pure salts and (Na, Rb) C$_2$H$_3$O$_2$ and (Na, Cs) C$_2$H$_3$O$_2$ molten mixtures are reported. Deviations from additivity for the $F_m$, $A_e$ and $E_x$ values are explained. The results for X$_2$H$_3$O$_2$ where X = Na, K, Rb, Cs and for (Na, X) C$_2$H$_3$O$_2$, where X = K, Rb, Cs are discussed.

Several properties of the alkali metal acetates were recently investigated by a number of authors $^1$-$^8$. In particular, the enthalpies and entropies of fusion and the cryoscopic constants were determined by our group $^5$-$^8$. More information on the electric conductivities, densities and activation energies at various temperatures for pure RbC$_2$H$_3$O$_2$ and CsC$_2$H$_3$O$_2$ and for the mixtures (Na, Rb) C$_2$H$_3$O$_2$ and (Na, Cs) C$_2$H$_3$O$_2$ is given in the present paper together with some considerations deduced by comparing the results of the mixtures (Na, X) C$_2$H$_3$O$_2$, where X = K, Rb, Cs.

Experimental

C. Erba RP Sodium Acetate and Nitrate (m. p. 601.0 K and 579.2 K, respectively), K & K 99% Rubidium Acetate (m. p. 514.0 K) and Merck “suprapur” Cesium acetate (m. p. 467.0 K), carefully dried under vacuum at 393 K, were used without further purification.

The conductance cell and the experimental procedure employed for the conductivity measurements were described previously $^8$. The apparatus for the density measurements is shown in Figure 1. It consists of a Pyrex glass vessel (a) provided with a long neck and a Pt-contact, a brass cylinder (b) with a drawing out cover (b') containing the Pyrex vessel, a furnace (c) controlled by a Chromel-Alumel thermocouple dipped in (d) and connected with a Leeds and Northrup CAT control unit, a second thermocouple, checked by comparison with a certified Pt resistance thermometer, which is put down in (e) and connected with a Solartron type LM 1420.2 digital voltmeter for the measurement of the melt temperature, a gauge (f) with a nonius (g) supplied with a quartz rod (h) carrying a Pt-contact for sensing the surface of the melt in (a), a microamperometer (i) and finally a metallic cover (l) acting as level reference of the height before the measurements. The apparatus was calibrated with NaN$_3$ by employing the density data given in $^9$.

Results

The experimental conductivities, $K$, linearly dependent on the temperature $T$ according to the equation:

$$K = -a + bT$$  \( (1) \)

are shown in Figure 2.
The values of the parameters $a$ and $b$ are summarized in Table I and, as described previously, may be represented by the polynomials

$$a = a_0 + a_1 x + a_2 x^2; \quad b = b_0 + b_1 x + b_2 x^2$$

(2)

where $x$ is the molar fraction of $\text{NaC}_2\text{H}_3\text{O}_2$.

The values of the parameters of the Eq. (2) are reported in Table II.

The difference between $K_{\text{exp}}$ and $K_{\text{calc}}$ is always less than 1%.

The experimental molar volumes of the two systems at fixed compositions up to 620 K together with the corresponding linear temperature dependences

$$V_m = m + qT$$

(3)

are reported in Figure 3.
Table II. Parameters of Equation (2) in units $\Omega^{-1} \cdot \text{cm}^{-1}$ and $\Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{K}^{-1}$ respectively.

<table>
<thead>
<tr>
<th>System</th>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$b_0 \cdot 10^3$</th>
<th>$b_1 \cdot 10^3$</th>
<th>$b_2 \cdot 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{Na, Rb})\text{C}_2\text{H}_3\text{O}_2$</td>
<td>0.7515</td>
<td>-0.02689</td>
<td>-0.07939</td>
<td>1.618</td>
<td>-0.1552</td>
<td>-0.08356</td>
</tr>
<tr>
<td>$(\text{Na, Cs})\text{C}_2\text{H}_3\text{O}_2$</td>
<td>0.6100</td>
<td>-0.1749</td>
<td>0.2139</td>
<td>1.415</td>
<td>-0.5155</td>
<td>0.4875</td>
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</tbody>
</table>

The values of the parameters of Eq. (3) are summarized in Table III. The apparent activation energies $E_A$ were determined by plotting $\log \Lambda_e$ vs. $10^3/T$ (see Fig. 4).

Table III. Parameters of Equation (3).

<table>
<thead>
<tr>
<th>System</th>
<th>$m$</th>
<th>$q \cdot 10^9$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{Na, Rb})\text{C}_2\text{H}_3\text{O}_2$</td>
<td>42.2836</td>
<td>3.741</td>
</tr>
<tr>
<td>0.75</td>
<td>47.3622</td>
<td>3.435</td>
</tr>
<tr>
<td>0.50</td>
<td>48.1136</td>
<td>3.677</td>
</tr>
<tr>
<td>0.25</td>
<td>52.6480</td>
<td>3.326</td>
</tr>
<tr>
<td>0.00</td>
<td>52.9450</td>
<td>3.643</td>
</tr>
<tr>
<td>$(\text{Na, Cs})\text{C}_2\text{H}_3\text{O}_2$</td>
<td>42.2836</td>
<td>3.741</td>
</tr>
<tr>
<td>0.75</td>
<td>56.2997</td>
<td>2.228</td>
</tr>
<tr>
<td>0.50</td>
<td>61.0004</td>
<td>2.199</td>
</tr>
<tr>
<td>0.20</td>
<td>64.7833</td>
<td>2.509</td>
</tr>
<tr>
<td>0.00</td>
<td>63.3688</td>
<td>3.331</td>
</tr>
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</table>

Table IV. $\Lambda_e$ values at fixed compositions and temperatures.

<table>
<thead>
<tr>
<th>System</th>
<th>$T$/K</th>
<th>$\Lambda_e$/ohm$^{-1}$ cm$^2$/mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{Na, Rb})\text{C}_2\text{H}_3\text{O}_2$</td>
<td>602</td>
<td>12.01</td>
</tr>
<tr>
<td>0.75</td>
<td>605</td>
<td>12.30</td>
</tr>
<tr>
<td>0.50</td>
<td>608</td>
<td>12.58</td>
</tr>
<tr>
<td>0.00</td>
<td>611</td>
<td>12.88</td>
</tr>
<tr>
<td>0.20</td>
<td>614</td>
<td>13.17</td>
</tr>
<tr>
<td>0.00</td>
<td>617</td>
<td>13.46</td>
</tr>
<tr>
<td>0.75</td>
<td>620</td>
<td>13.76</td>
</tr>
<tr>
<td>$(\text{Na, Cs})\text{C}_2\text{H}_3\text{O}_2$</td>
<td>602</td>
<td>12.01</td>
</tr>
<tr>
<td>0.75</td>
<td>605</td>
<td>12.30</td>
</tr>
<tr>
<td>0.50</td>
<td>608</td>
<td>12.58</td>
</tr>
<tr>
<td>0.20</td>
<td>611</td>
<td>13.17</td>
</tr>
<tr>
<td>0.00</td>
<td>614</td>
<td>13.46</td>
</tr>
<tr>
<td>0.75</td>
<td>617</td>
<td>13.76</td>
</tr>
<tr>
<td>0.50</td>
<td>620</td>
<td>14.00</td>
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</table>

The apparent activation energies $E_A$ were determined by plotting $\log \Lambda_e$ vs. $10^3/T$ (see Fig. 4).
Table V. Parameters of Eq. (4) and $E_A$ values.

<table>
<thead>
<tr>
<th>System</th>
<th>Molar fraction of NaC$_2$H$_3$O$_2$</th>
<th>$A$</th>
<th>$B$/K</th>
<th>$E_A$/kcal·mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Na, Rb) C$_2$H$_3$O$_2$</td>
<td>1.00</td>
<td>3.1123</td>
<td>-1.2236</td>
<td>5.60</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>3.1577</td>
<td>-1.2512</td>
<td>5.73</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>3.2242</td>
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<tr>
<td></td>
<td>0.25</td>
<td>3.2188</td>
<td>-1.2285</td>
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</tr>
<tr>
<td></td>
<td>0.00</td>
<td>3.1911</td>
<td>-1.1850</td>
<td>5.42</td>
</tr>
<tr>
<td>(Na, Cs) C$_2$H$_3$O$_2$</td>
<td>1.00</td>
<td>3.1123</td>
<td>-1.2236</td>
<td>5.60</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>2.9982</td>
<td>-1.1339</td>
<td>5.19</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>2.9154</td>
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<td>4.85</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>2.8830</td>
<td>-0.9885</td>
<td>4.52</td>
</tr>
<tr>
<td></td>
<td>0.00</td>
<td>2.9139</td>
<td>-0.9685</td>
<td>4.43</td>
</tr>
</tbody>
</table>

and determining the slopes $B$ of the corresponding linear relationships:

$$\log A_e = A + B \, 10^3/T.$$  \hspace{1cm} (4)

The values of $A$, $B$ and $E_A$ and the dependence of $E_A$ on the compositions are reported in Table V and Fig. 5, respectively. It can be noted that our $E_A$ value for sodium acetate is by $\sim 1.7\%$ higher than that calculated from literature data.

**Discussion**

The molar volumes, $V_m$, in the (Na, Cs) C$_2$H$_3$O$_2$ system are additive, while in the (Na, Rb) C$_2$H$_3$O$_2$ system there is a small positive deviation at 611 K and at various compositions (Figure 6).

Hazlewood et al. reported for the (Na, K) C$_2$H$_3$O$_2$ system a considerable positive deviation of the molar volumes.

Evidently the difference of the cation sizes in the melt influences the additivity law of the molar volume: in fact, the smaller the difference the higher the deviation.

In Fig. 7 the $A_e$ values are plotted vs. the composition of the mixtures, at 620 K, for the (Na, Cs) C$_2$H$_3$O$_2$ and (Na, Rb) C$_2$H$_3$O$_2$ systems.

The negative deviation from additivity is remarkable, as it was for the (Na, K) C$_2$H$_3$O$_2$ system studied earlier. This behaviour is explicable by considering the melt structure. In fact, even though these melts show disordering as compared to the regular crystal lattice, they can be considered as quasi-crystalline. It can be assumed that the acetate anions form a
cubic close-packed lattice and that the sodium ions are sufficiently small to fit into the interstices, without distorting the structure. It may be considered that the sodium ions, owing to their high charge density, are electrostatically bound to the anions and thus get out partially of the conductivity process.

Plotting the $\Lambda_e$ values of the $XC_2H_3O_2$ (where $X = Na, K, Rb, Cs$) pure melts vs. $T/T_{fus}$, one would expect at the reference temperature (i.e. 20 K above the respective melting points) a decrease of $\Lambda_e$ from sodium to cesium acetate (Figure 8). In reality the $\Lambda_e$ value of sodium acetate is lower than that of potassium acetate. This anomalous behaviour is explicable, as mentioned above, by the small size of the Na$^+$ as compared to the K$^+$ ion.

The $E_A$ values in the $(Na, Rb) C_2H_3O_2$ mixtures show positive deviations from additivity as expected from the negative deviation of the equivalent conductivity (Figure 5). On the contrary, the $(Na, Cs) C_2H_3O_2$ and the $(Na, K) C_2H_3O_2$ systems present a negative deviation of the apparent activation energy, $E_A$, in spite of the negative deviation of the corresponding equivalent conductivity.

In Fig. 9 the apparent activation energies, $E_A$, of pure molten $XC_2H_3O_2$ (where $X = Na, K, Rb, Cs$) melts are plotted vs. the cation radius. The $E_A$ values are higher for the sodium and potassium acetates than for the rubidium and cesium acetates.

In fact an increase of the ionic radius diminishes the $E_A$ due to the decrease of the ionic interactions in the melt.