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

Dante Leonesi, Augusto Cingolani, and Gianfrancesco Berchiesi

Istituto Chimico della Università degli Studi, I-62032 Camerino

(Z. Naturforsch. **31 a**, 1609–1613 [1976]; received April 16, 1976)

The electric conductivities, densities and activation energies of $RbC_2H_3O_2$ and $CsC_2H_3O_2$ pure salts and (Na, Rb) $C_2H_3O_2$ and (Na, Cs) $C_2H_3O_2$ molten mixtures are reported. Deviations from addivity for the V_m, Λ_e and E_Λ values are explained. The results for $X_2H_3O_2$ where X=Na, K, Rb, Cs and for (Na, X) $C_2H_3O_2$, 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 $RbC_2H_3O_2$ and $CsC_2H_3O_2$ and for the mixtures (Na, Rb) $C_2H_3O_2$ and (Na, Cs) $C_2H_3O_2$ is given in the present paper together with some considerations deduced by comparing the results of the mixtures (Na, X) $C_2H_3O_2$, 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 quarz 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 $NaNO_3$ by employing the density data given in [9].

Reprints request to Dr. Dante Leonesi, Istituto Chimico della Università degli Studi, Via S. Agostino, 1–*I-62032 Camerino.*

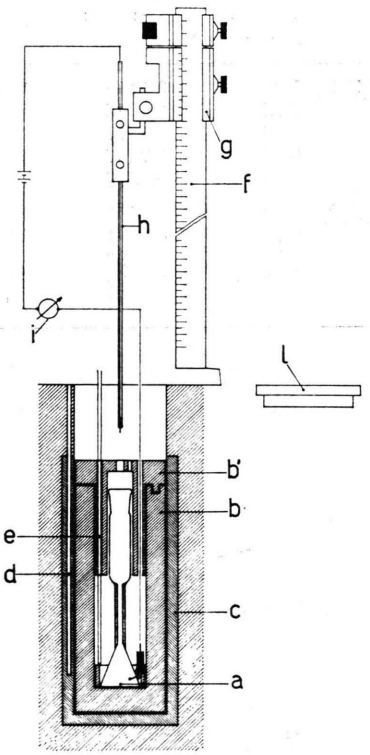

Fig. 1. The apparatus for density measurements.

Results

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

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

are shown in Figure 2.

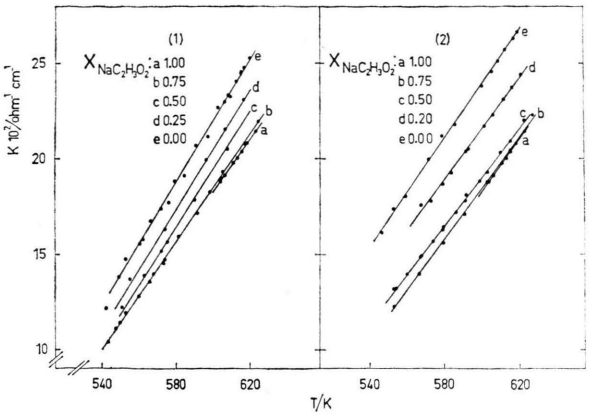

Fig. 2. The conductivity data for the systems. (1) (Na, Rb) $C_2H_3O_2$; (2) (Na, Cs) $C_2H_3O_2$.

Table I. Parameters of Equation (1).

System	Molar fraction of $NaC_2H_3O_2$	a Ω^{-1} cm^{-1}	$b\times10^3$ Ω^{-1} cm^{-1} K^{-1}
(Na, Rb) $C_2H_3O_2$	1.00	0.6449	1.379
	0.75	0.6876	1.456
	0.50	0.7177	1.520
	0.25	0.7397	1.573
	0.00	0.7517	1.619
(Na, Cs) $C_2H_3O_2$	1.00	0.6449	1.379
	0.75	0.6091	1.322
	0.50	0.5708	1.268
	0.20	0.5802	1.326
	0.00	0.6129	1.420

The values of the parameters a and b are summarized in Table I and, as described previously [8], may be represented by the polynomials

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

where x is the molar fraction of $NaC_2H_3O_2$.

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

The difference between $K_{exp.}$ and $K_{calc.}$ 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

$$V_m = m + q\,T \qquad (3)$$

are reported in Figure 3.

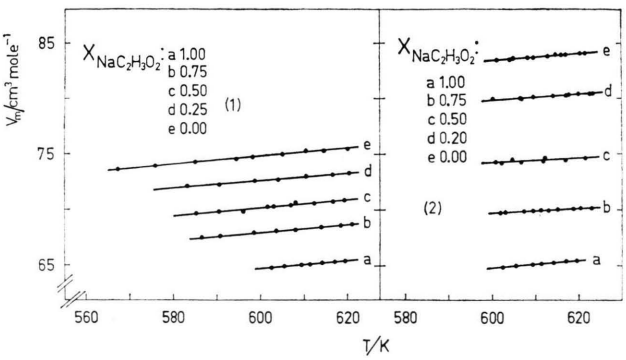

Fig. 3. The molar volume data for the systems. (1) (Na, Rb) $C_2H_3O_2$; (2) (Na, Cs) $C_2H_3O_2$.

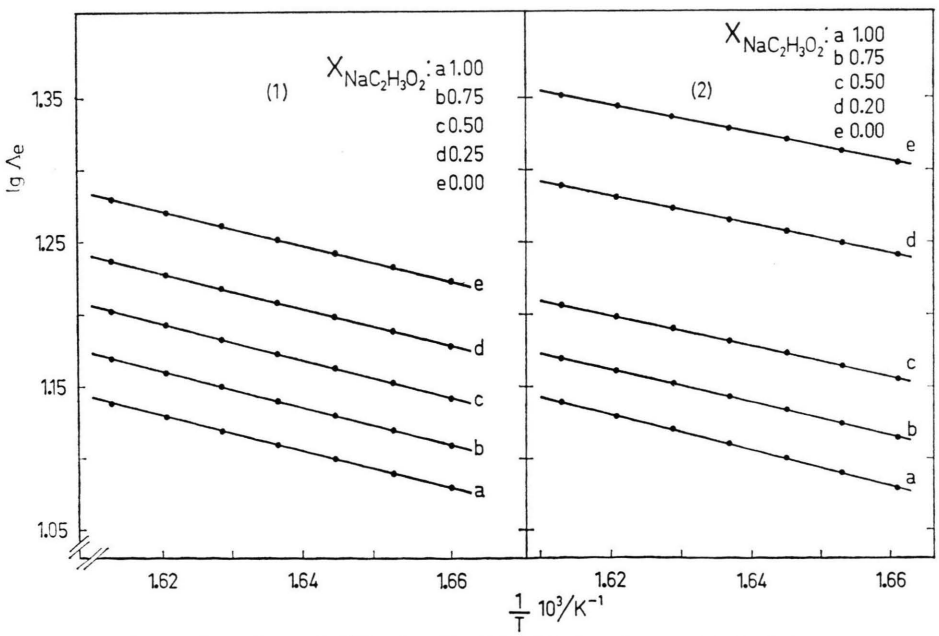

Fig. 4. Log Λ_e vs. $10^3/T$; (1) (Na, Rb) $C_2H_3O_2$; (2) (Na, Cs) $C_2H_3O_2$.

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

System	a_0	a_1	a_2	$b_0\cdot 10^3$	$b_1\cdot 10^3$	$b_2\cdot 10^3$
(Na, Rb) $C_2H_3O_2$	0.7515	−0.02689	−0.07939	1.618	−0.1552	−0.08356
(Na, Cs) $C_2H_3O_2$	0.6100	−0.1749	0.2139	1.415	−0.5155	0.4875

The values of the parameters of Eq. (3) are summarized in Table III. Table IV shows values of the equivalent conductance Λ_e calculated at given temperatures and compositions.

The apparent activation energies E_Λ, were determined by plotting $\log \Lambda_e$ vs. $10^3/T$ (see Fig. 4)

Table III. Parameters of Equation (3).

System	Molar fraction of $NaC_2H_3O_2$	m $cm^3\,mole^{-1}$	$q\cdot 10^2$ $cm^3K^{-1}mole^{-1}$
(Na, Rb) $C_2H_3O_2$	1.00	42.2836	3.741
	0.75	47.3622	3.435
	0.50	48.1136	3.677
	0.25	52.6480	3.326
	0.00	52.9450	3.643
(Na, Cs) $C_2H_3O_2$	1.00	42.2836	3.741
	0.75	56.2997	2.228
	0.50	61.0004	2.199
	0.20	64.7833	2.509
	0.00	63.3688	3.331

Table IV. Λ_e values at fixed compositions and temperatures.

System	Molar fraction of $NaC_2H_3O_2$	T/K	Λ_e/ohm^{-1} $cm^2\,mole^{-1}$
(Na, Rb) $C_2H_3O_2$	1.00	602	12.01
		605	12.30
		608	12.58
		611	12.88
		614	13.17
		617	13.46
		620	13.76
	0.75	602	12.85
		605	13.17
		608	13.49
		611	13.81
		614	14.13
		617	14.45
		620	14.77
	0.50	602	13.86
		605	14.21
		608	14.55
		611	14.89
		614	15.24
		617	15.58
		620	15.93

Table IV (continued)

System	Molar fraction of $NaC_2H_3O_2$	T/K	Λ_e/ohm^{-1} $cm^2\,mole^{-1}$
(Na, Rb) $C_2H_3O_2$	0.25	602	15.06
		605	15.43
		608	15.79
		611	16.16
		614	16.52
		617	16.89
		620	17.26
	0.00	602	16.69
		605	17.08
		608	17.47
		611	17.86
		614	18.26
		617	18.64
		620	19.04
(Na, Cs) $C_2H_3O_2$	1.00	602	12.01
		605	12.30
		608	12.58
		611	12.88
		614	13.17
		617	13.46
		620	13.76
	0.75	602	13.01
		605	13.20
		608	13.60
		611	13.88
		614	14.18
		617	14.47
		620	14.76
	0.50	602	14.29
		605	14.59
		608	14.88
		611	15.18
		614	15.48
		617	15.78
		620	16.08
	0.20	602	17.42
		605	17.75
		608	18.09
		611	18.43
		614	18.76
		617	19.09
		620	19.43
	0.00	602	20.18
		605	20.56
		608	20.95
		611	21.32
		614	21.71
		617	22.09
		620	22.48

Table V. Parameters of Eq. (4) and E_Λ values.

System	Molar fraction of $NaC_2H_3O_2$	A	B/K	E_Λ/kcal·mole^{-1}
(Na, Rb) $C_2H_3O_2$	1.00	3.1123	−1.2236	5.60
	0.75	3.1877	−1.2512	5.73
	0.50	3.2242	−1.2534	5.74
	0.25	3.2188	−1.2285	5.62
	0.00	3.1911	−1.1850	5.42
(Na, Cs) $C_2H_3O_2$	1.00	3.1123	−1.2236	5.60
	0.75	2.9982	−1.1339	5.19
	0.50	2.9154	−1.0596	4.85
	0.20	2.8830	−0.9885	4.52
	0.00	2.9139	−0.9685	4.43

and determining the slopes B of the corresponding linear relationships:

$$\log \Lambda_e = A + B\, 10^3/T\,. \qquad (4)$$

The values of A, B and E_Λ and the dependence of E_Λ on the compositions are reported in Table V and Fig. 5, respectively. It can be noted that our E_Λ value for sodium acetate is by $\sim 1.7\%$ higher than that calculated from literature data [8].

Discusion

The molar volumes, V_m, in the (Na, Cs) $C_2H_3O_2$ system are additive, while in the (Na, Rb) $C_2H_3O_2$ system there is a small positive deviation at 611 K and at various compositions (Figure 6).

Hazlewood et al.[1] reported for the (Na, K) $C_2H_3O_2$ 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 Λ_e values are plotted vs. the composition of the mixtures, at 620 K, for the (Na, Cs) $C_2H_3O_2$ and (Na, Rb) $C_2H_3O_2$ systems.

The negative deviation from additivity is remarkable, as it was for the (Na, K) $C_2H_3O_2$ system studied earlier[8]. 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

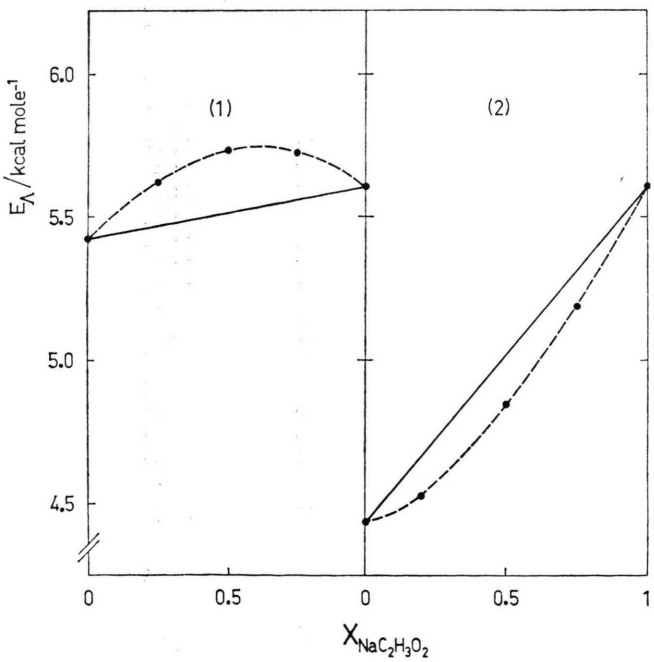

Fig. 5. The activation energy as a function of the $NaC_2H_3O_2$ molar fraction. (1) (Na, Rb) $C_2H_3O_2$; (2) (Na, Cs) $C_2H_3O_2$.

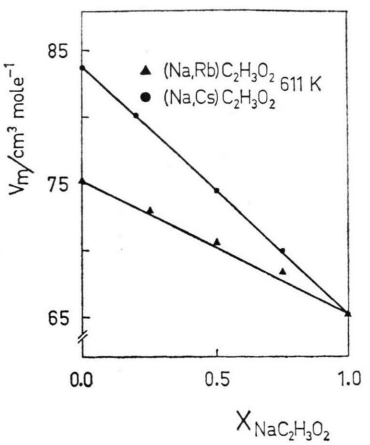

Fig. 6. The molar volume values vs. $NaC_2H_3O_2$ molar fraction.

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.

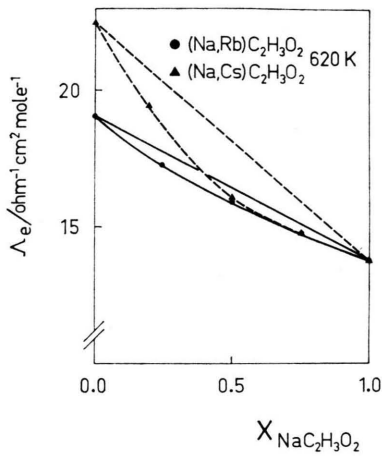

Fig. 7. The Λ_e values vs. the $NaC_2H_3O_2$ molar fraction at 620 K.

Plotting the Λ_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 [10]) a decrease of Λ_e from sodium to cesium acetate (Figure 8). In reality the Λ_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_Λ 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) $C_2H_3O_2$ [8] systems present a negative deviation of the apparent activation energy, E_Λ, in spite of the negative deviation of the corresponding equivalent conductivity.

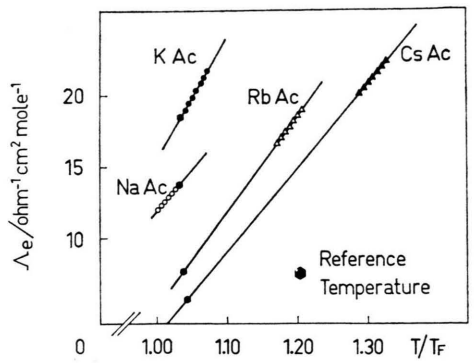

Fig. 8. The Λ_e values of Na, K, Rb and Cs acetates vs. T/T_{fus}.

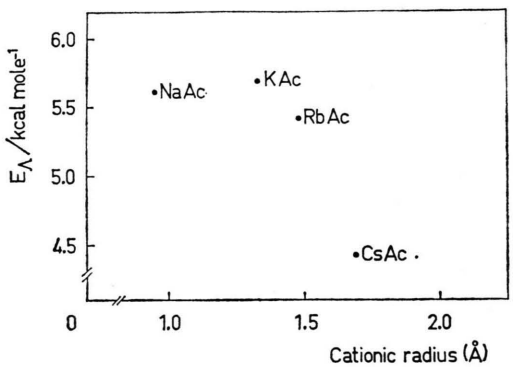

Fig. 9. The dependence of the activation energy on the cation radius, for Na, K, Rb, Cs acetates.

In Fig. 9 the apparent activation energies, E_Λ, of pure molten $XC_2H_3O_2$ (where X = Na, K, Rb, Cs) melts are plotted vs. the cation radius. The E_Λ 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_Λ due to the decrease of the ionic interactions in the melt.

[1] F. Hazlewood, E. Rhodes, and A. R. Ubbelohde, Trans. Faraday Soc. **62,** 3101 [1966].
[2] V. I. Yakerson, Izv. Acad. Nauk SSSR Otd. Khim. Nauk 1003 [1967].
[3] A. R. Ubbelohde, J. Chim. Phys. **66** [1969], 19th Meeting Supplement 59.
[4] Z. Halmos, T. Meisel, K. Seybold, and L. Erdey, Talanta **17,** 1191 [1970].
[5] M. Braghetti, D. Leonesi, and P. Franzosini, Ric. Sci. **38,** 116 [1968].
[6] G. Piantoni, D. Leonesi, M. Braghetti, and P. Franzosini, Ric. Sci. **38,** 127 [1968].
[7] M. Braghetti and G. Berchiesi, Ann. Meeting Chimica Inorganica 101 [1969].
[8] D. Leonesi, A. Cingolani, and G. Berchiesi, J. Chem. Eng. Data **18,** No. 4, 391 [1973].
[9] G. J. Janz, Molten Salts Handbook, Academic Press, New York 42 [1967].
[10] G. Morand and J. Hladik, Electrochimie des Sels Fondus I⁰, p. 113, Masson et Cie, Paris 1969.