Electric Conductivity of Sodium-Potassium Acetates Molten System

Dante Leonesi,[1] Augusto Cingolani, and Gianfrancesco Berchiesi
Istituto Chimico dell'Università di Camerino, 62032 Camerino, Italy

The conductivity (κ) in molten pure (Na, K)CH_3COO and in molten mixtures (Na, K)CH_3COO was measured. The variation of κ with the temperature (T) and of the mixtures' composition (x) is given by the empirical equation of the form:

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

The equivalent conductance (Λ) and the activation energy (E_Λ) were also calculated. Deviations from the ideality are shown.

Some thermodynamic properties of sodium and potassium acetates were discussed by our group previously (*2, 8*). In this paper we report the conductivity and the equivalent conductance of the molten pure (Na, K)CH_3COO and of the molten mixtures (Na, K)CH_3COO at various temperatures up to 620K.

Experimental

Chemicals. C. Erba RP sodium and potassium acetates (mp 601.0K and 578.5K, respectively), carefully dried, were used without further purification.

Measurements of temperature. The temperature of the melted mixtures contained in the conductance cell were measured by a Chromel-Alumel thermocouple. This thermocouple, checked by comparison with an NBS certified platinum resistance thermometer, was connected with a Solartron-type LM 1420.2 digital voltmeter.

The furnace temperature for the melting was controlled by a second thermocouple connected with a Leeds and Northrup CAT control unit. This thermocouple is dipped in the metallic core where the conductance cell is placed. This assembly stabilizes the melts temperature within ±0.20°C.

Measurements of conductance. The pyrex glass conductance cell reported by Howie and Macmillan (*4*) was conveniently modified by us (Figure 1). The conductance cell assembly consists of a test vessel and of a head, which supports electrodes, the sheath of the thermocouple, and the capillary, all extractable. Since the measurements were carried out in an inert gas atmosphere, dry nitrogen was bubbled through the melt.

Resistance measurements were carried out by an LKB precision bridge at a frequency of 2000 Hz after testing the independence of the resistance values from the frequency used (1000 and 2000 Hz). The cell constant (332.0 cm^{-1}) was determined by using $NaNO_3$ and KNO_3 C. Erba RP-ACS at various temperatures above the melting points up to 630K by the Janz parameters (*6*). This value remained constant during the measurements.

Results and Discussion

The phase diagram of the (Na, K)CH_3COO binary system was previously studied (*3, 5, 9*). The liquidus curve of this system substantially presents a simple eutectic at 508K ($x_{CH(3)COOK} = 0.537$) and a transition point at 513K ($x_{CH(3)COOK} = 0.615$).

The conductivity (κ) dependence with the composition (x) at fixed temperatures (602, 608, 614, and 620K) is shown in Figure 2. The isotherms obtained are smooth continuous curves showing no breaks.

In Figure 3 are reported the values of $\Delta\kappa$, i.e., the difference between the calculated by the additivity law and the experimental values, vs. x, at constant temperature. The highest deviations from the ideality occurred for mixtures of about 50% CH_3COOK.

The dependence of conductivity (κ) with the temperature (T) at the investigated compositions ($x_{CH(3)COOK}$ = 1; 0.75; 0.67; 0.60; 0.50; 0.25; 0.00) is reported in Figure 4 for each set of data. In every case, by use of the least-squares method, an equation of the first degree was determined:

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

The values of the parameters a and b are summarized in Table I.

To obtain the complete equation connecting the conductivity with the composition and the temperature, the parameters a and b of Equation 1 were plotted against the composition. By the least-squares method the dependence of the parameters a and b with the composition was calculated, and the obtained functions were substituted in Equation 1.

An equation of the following form fitted the data:

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

Values of the parameters are reported in Table II.

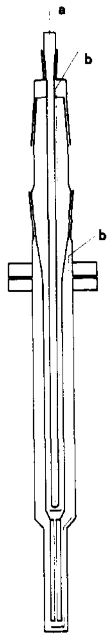

Figure 1. Conductance cell
a: Thermocouple
b: Electrodes

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[1] To whom correspondence should be addressed.

The deviation between the values of κ experimental and κ computed by means of Equation 2 is always less than 1%. Hazlewood et al. (*3*) measured the molar volume at various compositions of the (Na, K) acetate mixtures. By use of these values and Equation 2, we obtained the equivalent conductance (Λ) at several temperatures at fixed composition. The results are summarized in Table III.

The (Na, K)CH_3COO mixtures did not exhibit ideal behavior, according to Evan's definition (*7*). The Λ_{obsd} values in fact present a negative deviation from the Λ_{calcd} by use of the additivity law over the temperature range (602–620K). On the other hand, this could be expected (*1*) since the binary mixtures show "a considerable positive excess volume" (*3*).

The apparent activation energy (E_Λ) was determined by the Arrhenius equation, plotting log Λ vs. $1/T$ for the pure salts and for the different mixtures. The E_Λ values

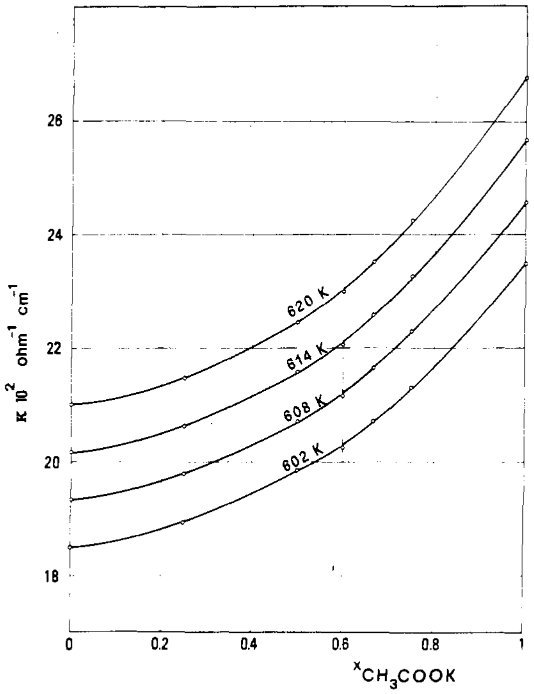

Figure 2. Conductivity dependence with CH_3COOK molar fraction at fixed temperatures

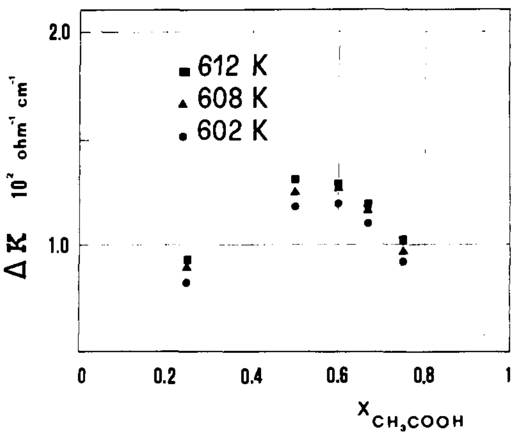

Figure 3. $\Delta\kappa$ ($\Delta\kappa_{theor} - \kappa_{exptl}$) dependence with CH_3COOK molar fraction

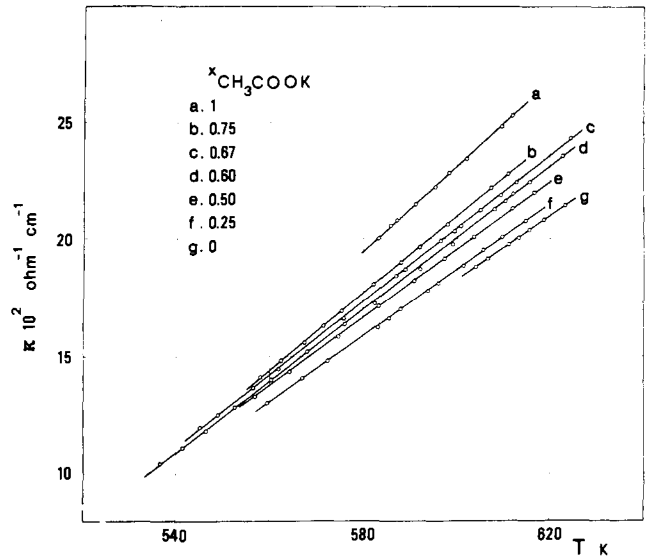

Figure 4. Conductivity variation with temperature at fixed compositions

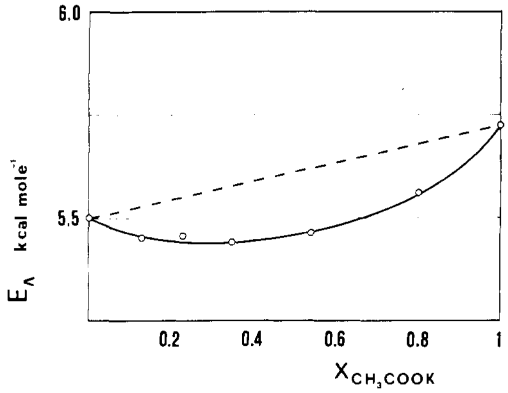

Figure 5. Activation energy as function of CH_3COOK molar fraction

Table I. Parameter Values of Equation 1

x_{CH_3COOK}	a	$b \cdot 10^3$
0.00	0.6449	1.3788
0.25	0.6545	1.4019
0.50	0.6713	1.4488
0.60	0.7127	1.5200
0.67	0.7270	1.5519
0.75	0.7715	1.6355
1.00	0.8506	1.8032

Table II. Parameter Values of Equation 2

a_0	0.6447	a_1	0.001379
b_0	0.0423	b_1	0.00006936
c_0	0.2534	c_1	0.0005013

Table III. Λ_{calcd} Values at Fixed Compositions and Temperatures

	Λ_{calcd} ($ohm^{-1} \cdot cm^2$)						
x_{CH_3COOK}	602K	605K	608K	611K	614K	617K	620K
1.000	19.0	19.5	19.9	20.4	20.9	21.3	21.8
0.7947	17.0	17.4	17.8	18.3	18.7	19.1	19.5
0.5370	15.3	15.6	16.0	16.3	16.7	17.1	17.4
0.3523	14.4	14.8	15.1	15.4	15.8	16.1	16.5
0.2276	14.0	14.4	14.7	15.0	15.4	15.7	16.0
0.1263	13.8	14.1	14.4	14.8	15.1	15.4	15.7
0.000	13.6	13.9	14.2	14.5	14.9	15.2	15.5

Table IV. E_A Values at Fixed Compositions

x_{CH_3COOK}	E_A, kcal/mol
1.0000	5.69
0.7947	5.56
0.5370	5.46
0.3523	5.44
0.2276	5.46
0.1263	5.45
0.000	5.50

were computed from the slopes of these plots that, in the temperature range considered, do not present a detectable curvature. The results are summarized in Table IV. The plot of these E_A values against compositions shows, contrary to any expectation, a negative deviation from ideality (Figure 5).

Acknowledgment

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Simple Technique to Determine Solubilities of Sparingly Soluble Organics: Solubility and Activity Coefficients of *d*-Limonene, *n*-Butylbenzene, and *n*-Hexyl Acetate in Water and Sucrose Solutions

Hugo A. Massaldi[1] **and C. Judson King**[2]
Department of Chemical Engineering, University of California, Berkeley, Calif. 94720

Head-space analysis by gas-liquid chromatography is used to determine solubilities of sparingly soluble substances of significant volatility. This technique is based on the analysis of the vapor phase in equilibrium with a liquid to which increasing microquantities of the solute have been fed in different flasks. The value of the pure solute vapor pressure is required. Solubility and activity coefficients of *d*-limonene, not available heretofore, are determined by this method at 0°, 5°, and 25°C in 0, 20, and 40% aqueous sucrose solutions and at 25°C in 60% sucrose. The reliability of the technique is confirmed by determining the solubility of *n*-butylbenzene and *n*-hexyl acetate at 25°C in water. Results for *n*-butylbenzene compare well with existing data, and for *n*-hexyl acetate, improved agreement with the hydrogen bond energy parameter is obtained. Activity coefficients of *d*-limonene and *n*-butylbenzene decrease with increasing sucrose concentration, whereas opposite behavior is obtained for *n*-hexyl acetate. The heats of solution of *d*-limonene in water and 40% sucrose solution are derived from the results.

Data on solubilities of relatively insoluble substances are scarce, partly because of lack of interest but mainly because of difficulties in obtaining reliable results. However, these data are increasingly needed in such diverse fields as water pollution control, biology, toxicology, and food processing. In particular, in the concentration and drying of citrus juices, an important question is how much of the substances responsible for the aroma and flavor is fully dissolved at different temperatures in solutions of varying sugar contents. *d*-Limonene, a substance critical to the aroma and flavor of citrus juices, constitutes between 70 and 90% of the essential oil present in natural citrus juices as a second phase. No data on solubility of this substance and no correlations appropriate for estimating its activity coefficient were found in the literature.

Spectrophotometry of saturated solutions was used by Andrews and Keefer (*2*), Bohon and Claussen (*4*), Klevens (*9*), and recently by Wauchope and Getzen (*14*) to determine solubilities of several liquid and solid hydrocarbons in water. Analysis by gas-liquid chromatography (glc) of liquid samples of a saturated water solution relative to a standard solution of the solute in an organic solvent was used by Buttery et al. (*5*) and McAuliffe (*11*) to determine the solubility of some slightly soluble volatiles. All these methods require separation of phases after the saturation step, by either siphoning or extraction or centrifugation. This handling of the solution can introduce error, particularly for liquid solutes or for experiments at temperatures other than ambient.

Buttery et al. (*5*) also determined air-water partition coefficients of volatile solutes by glc analysis of vapor and liquid phases in equilibrium. Activity coefficients of a number of volatiles in sucrose solutions of different concentrations were measured by Chandrasekaran and King (*7*) by use of head-space analysis.

In this work a simple technique based on head-space analysis and glc was developed to determine solubilities and/or activity coefficients of sparingly soluble organics. Saturated solutions need not be prepared in advance, thereby avoiding the problems of phase separation, nor

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[1] Present address, Depto. De Technologia Quimica, Facultad De Ciencias Exactas (UNLP), Calle 47 y 115, La Plata, Argentina.
[2] To whom correspondence should be addressed.