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## ORIGINAL ARTICLE

# Comparative conductimetric studies of salicylic acid in methanol–water mixtures at 25 °C

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## KEYWORDS

Salicylic acid;  
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**Abstract** Conductivity data of salicylic acid in methanol–water mixtures were measured at 25 °C. The data were analyzed in two methods, the Hsia–Fuoss's and Fuoss 78's conductance equations and a comparison was made. The two methods concern the derivation of thermodynamic association constants and limiting molar conductivities for all solvent compositions. The limiting equivalent conductance decreases with the increase of methanol content in the binary mixtures over the whole range of the solvent composition, but the variation does not give a constant value of Walden product. The electrolytes were found to be practically completely associated in all studied solvent mixtures. The association constant of acid decreases with the increase in relative permittivity of the mixtures. The values of ionic coefficients of self diffusion and the ionic conductance at infinite solutions were estimated.

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## 1. Introduction

Salicylic acid (*o*-hydroxybenzoic acid) is a phenolic compound present in plants, it is an important intermediary in the production of aspirin, and its derivatives were also used in the

pharmaceutical and polymer industries for manufacture of disinfectants, antiseptics, and detergents (Khiati et al., 2007). Thermodynamic association constant values for salicylic acid in some alcohols and water solutions were derived potentiometrically (Grunwald and Berkowitz, 1951; Novák et al., 1997; Völgyi et al., 2007).

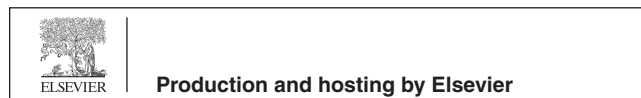
Literature reveals that there is little work on the conductimetric behavior of salicylic acid in these solvents mixtures (Bray et al., 1957; Dippy et al., 1964; Mandal and Lahiri, 1976; Papadopoulos and Avarans, 1991; Sadiq et al., 1993; Sadiq and Khan, 1993). We present in this paper the conductance data of salicylic acid at 25 °C in methanol–water mixtures in composition from 0 to 90.59 mass% of the co-solvent. Also we used the Hsia–Fuoss and Fuoss 78 equation to analyze

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the conductance–concentration data and to derive the thermodynamic association constants,  $K_A$ , the limiting molar conductivities,  $\Lambda_0$  and Walden product.

## 2. Experimental

Salicylic acid (*o*-hydroxybenzoic acid, puriss. p.a.,  $\geq 99.5\%$  from Aldrich was used without purification), methanol (purity  $> 99\%$ ) and triply distilled water with the specific conductivity of  $0.5 \mu\text{S cm}^{-1}$  were used for the preparation of binary mixtures. Densities of the mixtures were determined in a 20 mL pycnometer at  $(25.00 \pm 0.05)^\circ\text{C}$ . Viscosities of the mixtures were measured with Falling Ball viscometer “Gilmont instruments” with 0.2–1% of precision. Solvent mixtures were made up by weight, the densities, viscosity and relative permittivity constants of mixed solvents are given in Table 1.

The conductance measurements were carried out for the prepared solutions using a conductimeter CDM230 (with 0.2% of precision) with the cellule CDC641T (comprising two platinized platinum electrodes) connected to an ultra-thermostat to maintain the temperature constant at the desired temperature ( $\pm 0.05^\circ\text{C}$ ).

All solutions were made up by weight and volume concentrations in mole per liter by gradual dilution were calculated using the densities of the solvents. The molar conductivities,  $\Lambda$ , were calculated from the experimental electrolytic conductivities after correcting for the electrolytic conductivity of the pure solvent.

## 3. Data analysis

The experimental data were analyzed with Fuoss and Hsia (1967) and Fuoss 78 conductance equation (Fuoss, 1978).

### 3.1. Hsia–Fuoss method

For the partially dissociated (1:1) electrolytes Hsia and Fuoss proposed that:

$$\Lambda = \left[ \frac{\Lambda_0 - S\sqrt{\gamma c} + E(\gamma c) \ln(\gamma c) + J_1(\gamma c) + J_2\sqrt{(\gamma c)^3}}{1 + K_A c \gamma^2} \right] \quad (1)$$

The activity coefficient was calculated according to the reference (Kuba and Hawlicka, 2003):

**Table 1** Properties of the solvent mixtures (methanol–water) at  $25^\circ\text{C}$ .

Mass (%) $\text{CH}_3\text{OH}$	$\rho^a/\text{g m}^{-3}$	$\eta^b/\text{centipoises}$	$\epsilon_r^c$
0	0.996	0.891	78.48
19.79	0.971	1.526	69.85
37.54	0.934	1.572	61.50
49.97	0.919	1.569	55.76
72.55	0.869	1.356	45.32
90.59	0.822	1.033	36.63

<sup>a</sup> Density of solvents.

<sup>b</sup> Viscosity of solvents.

<sup>c</sup> Relative permittivity data incorporated in this table have been taken from the literature (Xue and Traina, 1996).

$$f = \exp \left[ - \frac{A\sqrt{\gamma c}}{1 + BR\sqrt{\gamma c}} \right] \quad (2)$$

with:

$$A = \frac{2.791 \times 10^6}{(\epsilon_r T)^{3/2}} \quad (3)$$

$$B = \frac{50.29}{(\epsilon_r T)^{1/2}} \quad (4)$$

$R$  is cosphere diameter,  $\gamma$  is the degree of dissociation,  $K_A$  is the association constant for ion pairs and  $f$  is the mean activity coefficient of the free ions. Other terms have their usual meanings.

$S$ ,  $E$ ,  $J_1$  and  $J_2$  were calculated using the equations given by Fernandez Prini (Prini, 1969).

The Eq. (1) is resolved for  $\Lambda_0$  and  $K_A$  which minimizes:

$$\sigma^2 = \sum_j [\Lambda_j(\text{calcd}) - \Lambda_j(\text{obsd})]^2 / (n - 3) \quad (5)$$

where  $n$  is the number of data points.

### 3.2. Fuoss 78 method

The limiting molar conductivity,  $\Lambda_0$ , and association constant,  $K_A$ , were deduced from the following equations:

$$\Lambda = p[\Lambda_0(1 + RX) + EL] \quad (6)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (7)$$

$$\ln f = - \frac{\beta k}{2(1 + kR)}, \quad \beta = \frac{e^2}{\epsilon_r kT} \quad (8)$$

which minimize the standard deviation:

$$\sigma^2 = \sum_j [\Lambda_j(\text{calcd}) - \Lambda_j(\text{obsd})]^2 / (n - 2) \quad (9)$$

For additional precision and since the  $H_2$  polynomials of Fuoss are not equal at the explicit form correspondent, the expressions for  $RX$  and  $EL$  in Eq. (6) are the explicit relaxation and hydrodynamic terms respectively (Fuoss, 1978).

## 4. Results and discussion

Conductivity data for salicylic acid in methanol–water mixtures ( $36.63 \leq \epsilon_r \leq 78.48$ ;  $0.891 \leq \eta \leq 1.572$  poises) were measured in the concentration range ( $2.2910^{-6} \leq c \leq 1.1210^{-2} \text{ mol L}^{-1}$ ) at  $25^\circ\text{C}$ . In the case of 90.59% of methanol the measures were unstable; hence we take the average value of conductivities.

For the two methods, no minimum is observed in  $R-\sigma\%$  plots in accordance with the Fuoss conclusion (Fuoss, 1978), the  $R$  values were used equal to the Bjerrum distance according to the suggestions of Justice and others (Justice, 1971; Sadiq et al., 1993; Papadopoulos and Avarans, 1991).

Ostwald law to estimate initial values of  $\Lambda_0$  and  $K_A$  was used. The conductance parameters of the acid: The molar conductance at infinite dilution,  $\Lambda_0$ , standard deviations  $\sigma\%$  based on the observed and calculated  $\Lambda$  values and acid association constants obtained by using the two methods are exhibited in Table 2.

**Table 2** Conductance parameters of the salicylic acid in methanol–water mixtures at 25 °C.

Equation <sup>a</sup>	$\Lambda_0/S\text{ cm}^2\text{ mol}^{-1}$	$10^{-3} K_A/\text{dm}^3\text{ mol}^{-1}$	$\sigma\%$	$R/A$
		% CH <sub>3</sub> OH		
		0%		
H–F	384.17	0.962	0.100	3.57
F78	386.06	1.004	0.024	3.57
		19.79%		
H–F	249.64	1.653	0.099	4.01
F78	249.99	1.699	0.002	4.01
		37.54%		
H–F	169.92	3.921	0.094	4.56
F78	170.03	4.000	0.022	4.56
		49.97%		
H–F	149.72	5.847	0.103	5.02
F78	150.16	6.013	0.054	5.02
		72.55%		
H–F	103.84	18.015	0.049	6.43
F78	105.45	19.126	0.042	6.43
		90.59%		
H–F	70.12	891.130	0.079	7.65
F78	70.29	900.887	0.076	7.65

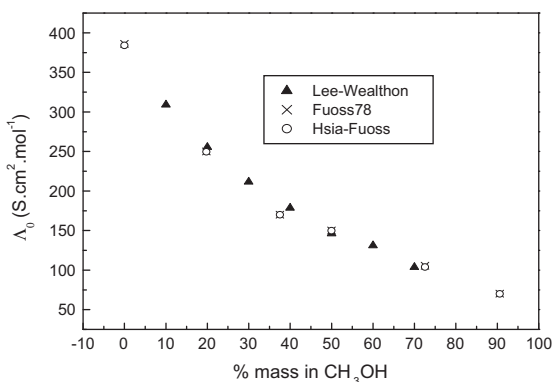
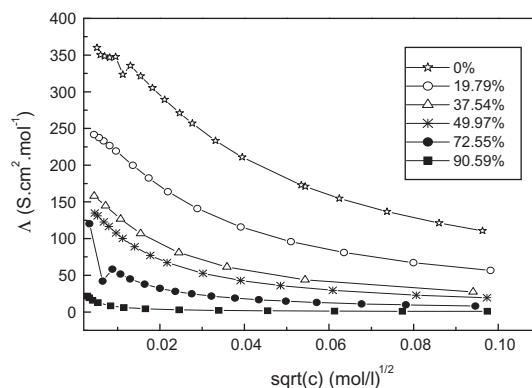
<sup>a</sup> H–F and F78 represent results obtained by using the Hsia–Fuoss and Fuoss 78 equations respectively.

Table 2 shows that  $\Lambda_0$  values were approximately similar; the limiting conductance for salicylic acid in aqueous solution calculated by H–F equation is in good agreement with the values 384.2 (Sadiq and Khan, 1993), 384.23 (Sadiq et al., 1993) reported in the literature using other methods of analysis.

The  $\Lambda_0$  values for salicylic acid in methanol water mixtures and those derived by using the Lee–Wheaton method (Sadiq et al., 1993) are compared (Fig. 1). The limiting equivalent conductance decreased with the increase in the contents of methanol in water suggesting the increased ion–solvent and solvent–solvent interactions.

Fig. 2 shows that the molar conductance for the acid decreases with the increase in the content of methanol in water and that is a result to the reduction of dissociates power of solvent tie in its relative permittivity. Less concentration conductance dependency is observed when the composition of methanol is more than 50%.

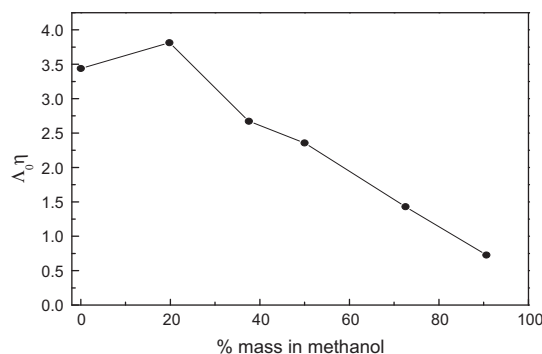
The  $\sigma\%$  values show that the F78 model describes the conductivity of the acid in water rich region of the mixtures better

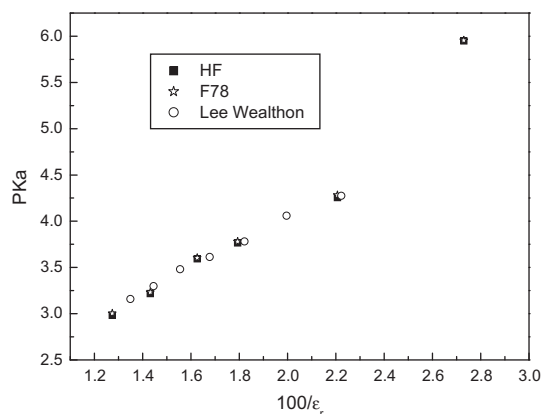
**Figure 1** Variation of the limiting equivalent conductance with composition of methanol.**Figure 2** Variation of the molar conductance for the acid with composition of the solvent mixtures at 25 °C.

than the HF model while they are comparable in methanol rich region of the mixtures. The difference between the  $K_A$  values calculated by application of the two methods increases with composition of methanol in the mixtures.

The variation of Walden product with composition of the solvent mixtures (Fig. 3) presents a maximum between 12–20 mol% methanol, as has been found in this binary mixture for various electrolytes (Broadwater and Kay, 1970; Broadwater and Kay, 1971, 1976). The presence of this maximum shows that the limiting conductance of the solutions decreases more slowly along with growing of the methanol content in the mixture than it would be expected from the increase of viscosity of the mixed solvents in water rich region. The constancy of the Walden product also fails in general for small ions in mixed solvents (D'Aprano and Fuoss, 1963, 1975; Fuoss, 1959; Hemms, 1974; Skinner and Fuoss, 1966; Zwanzig, 1963, 1970).

The dependence of the thermodynamic acid dissociation  $pK_a$  on the inverse of the solvents relative permittivity and a comparison of the values calculated by the H–F, F78 and Lee–Wheaton (Sadiq et al., 1993) methods are shown in Fig. 4. A similar variation was found for salicylic acid in water with other cosolvent mixtures such as ethanol (Mandal and Lahiri, 1976), 1-propanol (Papadopoulos and Avarans, 1991) and acetone (Sadiq et al., 1993). The  $pK_a$  in aqueous solutions calculated by the two methods is in agreement with those found by other analyzed methods (Bray et al., 1957; Dippy

**Figure 3** Variation of the Walden product with the composition of the solvent mixture.



**Figure 4** Dependence of  $Pk_a$  on the inverse of the dielectric constants.

et al., 1964; Papadopoulos and Avarans, 1991; Sadiq and Khan, 1993). The increased association on added methanol was interpreted by stabilization of anion with existence of an internal hydrogen bond formed between the carboxyl and hydroxyl groups (Bray et al., 1957; Dippy et al., 1964; Papadopoulos and Avarans, 1991).

The self diffusion coefficient of the proton  $D_+^0$  at infinite dilution was estimated from the work of Solntsev et al. 2000. The limiting conductance of proton  $\Lambda_0^+$  in the mixtures is calculated using the Nernst equation:

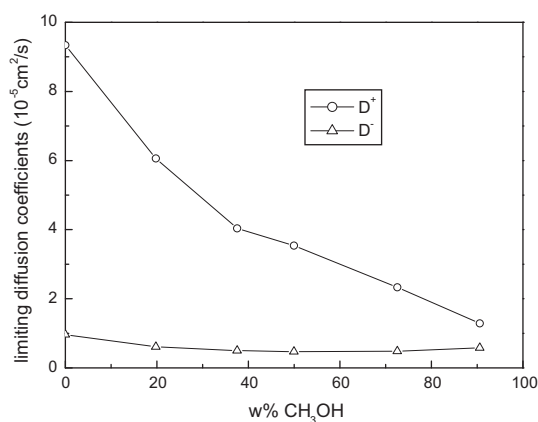
$$D_+^0 = \frac{R^*T}{F^2} \lambda_+^0 \quad (10)$$

$R^*$  and  $F$  denote gas and Faraday' constants, respectively. Our  $\Lambda_0^+$  values are in agreement with the values reported in the literature (Apelbat, 2008, 2011). The Kohlrausch equation for the independent motion of ions and the Eq. (10) allowed us to calculate the limiting conductivity and self-diffusion coefficient of salicylate ion  $D_-^0$  (Table 3). The influence of the solvent composition on the ion limiting self diffusion coefficients and limiting ionic conductivities in methanol–water mixtures are shown in Fig. 5 and Figs. 6 and 7 respectively. The limiting self-coefficient diffusion of salicylate lies beneath that of proton, this is due to lower mobility of the anion compared with the hydronium ion, and  $D_-^0$  varies slightly with relative permittivity than  $D_+^0$ .

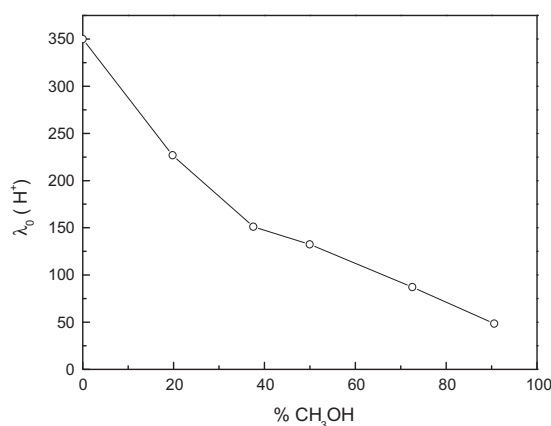
The variation of the limiting ionic conductivities (Fig. 6) and (Fig. 7) composition of methanol confirms that the interaction ion–solvent is very different for the two ions. Fig. 6

**Table 3** Walden product, ion limiting self-diffusion coefficient ( $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ), and limiting ionic conductivity ( $\text{S cm}^2 \text{ mol}^{-1}$ ) in methanol water mixtures at 25 °C.

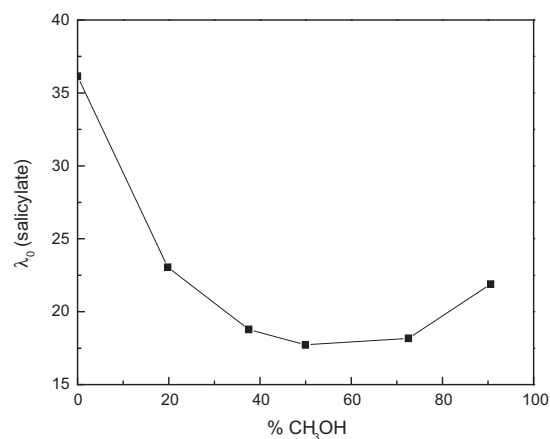
W% CH <sub>3</sub> OH	$\Lambda_0\eta$	$\Lambda_0^+$	$\Lambda_0^-$	$D_+^0$	$D_-^0$
0	3.44	349.92	36.14	9.34	0.96
19.79	3.81	226.94	23.05	6.06	0.61
37.54	2.67	151.24	18.79	4.04	0.50
49.97	2.36	132.43	17.73	3.54	0.47
72.55	1.43	87.28	18.17	2.33	0.48
90.59	0.73	48.46	21.89	1.29	0.58



**Figure 5** Limiting diffusion coefficient of proton and salicylate in water methanol mixtures.



**Figure 6** Variation of limiting conductance of proton with composition of methanol.



**Figure 7** Variation of limiting conductance of salicylate with composition of methanol.

shows that the decrease of  $\Lambda_0$  depends on the reduction of excess mobility of proton in adding the methanol in water.

The variation of limiting ionic conductance of salicylate with composition of methanol divided the solvent mixtures into two regions: the water rich region where this anion is more

stabilized by hydrogen bonding of the two solvents, and the methanol rich region where it becomes less solvated so its mobility is increased. By extrapolating this curve, we estimated the value of  $24.73 \text{ S cm}^2 \text{ mol}^{-1}$  of salicylate ion methanol.

## 5. Conclusions

Conductivity data of salicylic acid in methanol–water solution mixtures were obtained by using the two methods (Hsia–Fuoss and Fuoss78) at 25 °C. This study shows that the  $\Lambda_0$  variation with the composition of methanol in the mixtures is the same found by the H–F, F78 and Lee–Wheaton conductance equations while the association constant depends on the model than is the limited conductance. Until more data are available no conclusions will be drawn about the magnitudes of  $K_A$  values obtained here.

The  $\Lambda_0\eta$  does not show constancy with change in solvent composition indicating appreciable ion–solvent interactions.

The limiting conductance of salicylate in water methanol mixtures is sensitive to electrostatic and hydrodynamic interactions in this solution.

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