

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

Z. Chaaoui,<sup>a</sup> Ali H. Al-Taiar,<sup>b</sup> and Adil A. Othman<sup>b\*</sup>

<sup>a</sup>Department of Physics, Faculty of Sciences, University of Sciences and Technology of Oran "Mohamed Boudiaf", P.O.B. 1505 El M'naouar, 31003 Oran, Algeria.

Fax: 00213 4156 0353. E-mail: zahraaz@yahoo.com

<sup>b</sup>Department of Chemistry, Faculty of Sciences, University of Sciences and Technology of Oran "Mohamed Boudiaf", P.O.B. 1505 El M'naouar, 31003 Oran, Algeria.

Fax: 00213 4142 5763. E-mail: adelaliothman@gmail.com

The conductivity of salicylic acid in methanol–water mixtures was measured at 25 °C. Experimental data were analyzed using the Hsia–Fuoss and Fuoss–78 conductance equations and a comparison was made. The Hsia–Fuoss and Fuoss–78 methods were also used to determine the thermodynamic association constants and the limiting molar conductivities for all solvent compositions. The limiting equivalent conductance decreases with an increase in the methanol content in the binary mixtures over the whole range of solvent compositions, but the variation does not give a constant value of Walden product. The electrolytes were found to be practically completely associated in all solvent mixtures studied. The association constant of salicylic acid decreases as the dielectric constants of the mixtures increase.

**Key words:** salicylic acid, association constants, Walden product, electrolyte conductivity.

Salicylic acid (SA, *o*-hydroxybenzoic acid) is a phenolic compound present in plants. It is an important intermediate in the production of aspirin, and its derivatives are also used in pharmaceutical and polymer industries to manufacture disinfectants, antiseptics, and detergents. Thermodynamic association constant values of SA in some alcohol–water solutions were determined potentiometrically.<sup>1–3</sup>

There are a few studies on the conductometric behavior of SA in solvent mixtures.<sup>4–9</sup> In this paper, we present the conductance data of salicylic acid at 25 °C in methanol–water mixtures containing from 0 to 90.59 weight % of MeOH. To determine the thermodynamic association constants,  $K_A$ , the limiting molar conductivities,  $\lambda_0$ , and the Walden product values, the conductance–MeOH concentration data were analyzed using the Hsia–Fuoss and Fuoss–78 equations.

### Experimental

Salicylic acid (puriss. p.a., >99.5%, Aldrich) was used without purification. Methanol (purity > 99%) and triply distilled water with a specific conductivity of less than 1  $\mu\text{S cm}^{-1}$  was used for the preparation of binary mixtures. Densities of the mixtures were determined in a 20 mL pycnometer at 25.00±0.05 °C. Viscosities of the mixtures were measured with a Falling Ball viscometer (Gilmont Instruments) to an accuracy of 0.2–1%. The densities, viscosities, and dielectric constants of the solvent mixtures are listed in Table 1.

Conductivity measurements were carried out using a CDM230 conductivity meter (Radiometer Analytical SAS, France) equipped with a CDC641T cell comprising two platinized platinum electrodes. Taking into account the sources of error (calibration, measurements, impurities), the molar conductivity values are accurate to within 0.02%. During the experiments, the cell was calibrated using aqueous KCl solution at least five times and then immersed in a thermostat where the temperature was maintained with an accuracy  $\Delta T = \pm 0.05$  °C.

All solutions were made up by weight. The volume concentrations (in mol L<sup>-1</sup>) were calculated using the densities of the solvent mixtures. The molar conductivities,  $\lambda$ , were calculated

**Table 1.** Properties of methanol–water mixtures at 25 °C

$\alpha^a$	$\rho^b/\text{g cm}^{-3}$	$\eta^c/\text{P}$	$D^d$
0	0.9958	0.00891	78.48
19.79	0.9714	0.01526	69.85
37.54	0.9345	0.01572	61.50
49.97	0.9186	0.01569	55.76
72.55	0.8686	0.01356	45.32
90.59	0.8223	0.01033	36.63

<sup>a</sup> Weight fraction of MeOH (%).

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

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

<sup>d</sup> Data taken from Ref. 10.

from the experimental electrolyte conductivities corrected for the electrolyte conductivity of the pure solvent.

Experimental data were analyzed using the Hsia–Fuoss<sup>11</sup> and Fuoss-78<sup>12</sup> conductance equations.

The Hsia–Fuoss method is based on the assumption<sup>11</sup> that the conductance  $\lambda$  of a partially dissociated (1 : 1) electrolyte is related to its concentration  $c$ :

$$\lambda = [\lambda_0 - S(\gamma c)^{1/2} + E(\gamma c) \ln(\gamma c) + J_1(\gamma c) + J_2(\gamma c)^{3/2}]/(1 + K_A c f^2 \gamma), \quad (1)$$

where  $\gamma$  is the degree of dissociation,  $K_A$  is the association constant of ion pairs, and  $f$  is the mean activity coefficient of free ions.

The activity coefficient was calculated according to Ref. 13:

$$f = \exp\{-A(\gamma c)^{1/2}/[1 + BR(\gamma c)^{1/2}]\}, \quad (2)$$

where  $A = 2.791 \cdot 10^6 (DT)^{-3/2}$ ,  $B = 50.29 (DT)^{-1/2}$ ,  $R$  is the diameter of the Gurney cosphere of the ion,  $D$  is the dielectric constant, and  $T$  is absolute temperature.

The  $S$ ,  $E$ ,  $J_1$ , and  $J_2$  values were calculated using the known equations.<sup>14</sup>

Equation (1) is resolved for  $\lambda_0$  and  $K_A$  which minimize the standard deviation

$$\sigma^2 = \Sigma[\lambda_j^{\text{calc}} - \lambda_j^{\text{exp}}]^2/(n - 3), \quad (3)$$

where  $n$  is the number of data points.

The Fuoss-78 method. The limiting molar conductivity,  $\lambda_0$ , and the association constant,  $K_A$ , were deduced from the following equations:

$$\Lambda = p[\lambda_0(1 + RX) + EL], \quad (4)$$

$$\gamma = 1 - K_A c \gamma^2 f^2, \quad (5)$$

$$\ln f = -\beta \kappa/[2(1 + \kappa R)], \quad \beta = e^2(DkT)^{-1} \quad (6)$$

and then the standard deviation was minimized:

$$\sigma^2 = \Sigma(\lambda_j^{\text{calc}} - \lambda_j^{\text{exp}})^2/(n - 2). \quad (7)$$

The expressions for  $RX$  and  $EL$  in Eq. (4) are the explicit relaxation and hydrodynamic terms, respectively.<sup>12</sup>

## Results and Discussion

The conductivity of SA in methanol–water mixtures ( $36.63 \leq D \leq 78.48$ ;  $0.0089 \text{ P} \leq \eta \leq 0.0157 \text{ P}$ ) was measured at 25 °C in the concentration range  $2.29 \cdot 10^{-6} \text{ mol L}^{-1} \leq c \leq 1.12 \cdot 10^{-2} \text{ mol L}^{-1}$ . At a methanol concentration of 90.59%, the results were unstable; hence we take the average value of the conductivity.

Calculations by both methods revealed no minimum in  $R-\sigma\%$  plots in accordance with published data<sup>12</sup> ( $R$  values were used equal to the Bjerrum distance, see Refs 6, 8, and 15).

The initial  $\lambda_0$  and  $K_A$  values were estimated using the Ostwald law. The molar conductance of SA at infinite

dilution,  $\lambda_0$ , the standard deviations  $\sigma\%$  based on the observed and calculated  $\lambda$  values, and the SA association constants obtained using the two methods are listed in Table 2. From the data of Table 2 it follows that at methanol concentrations higher than 50%, the  $\sigma\%$  values found by the Hsia–Fuoss method are larger than those determined using the Fuoss-78 equation.

The  $\lambda_0$  values calculated by both methods are approximately equal. The limiting conductance of SA in aqueous solution calculated by the Hsia–Fuoss equation is in good agreement with the published data (384.2,<sup>9</sup> 385.2,<sup>4</sup> and 384.23 S cm<sup>2</sup> mol<sup>-1</sup> (see Ref. 6).

In Fig. 1, the  $\lambda_0$  values of SA in methanol–water mixtures are compared with those found earlier.<sup>9</sup> The limiting equivalent conductance decreases as the content of methanol in water increases, thus suggesting stronger ion–solvent and solvent–solvent interactions.

Figure 2 shows that the molar conductance of SA decreases with increasing the concentration of methanol in water as a result of reduction of the dissociative power of the solvent. At methanol concentrations above 50%, smaller conductance variations are observed.

The plot of the Walden product vs. composition of the solvent mixtures (Fig. 3) passes through a maximum between 12 and 20% of methanol, as was found in this binary mixture for various electrolytes.<sup>16–18</sup> The presence of this maximum shows that the limiting conductance of the solutions decreases more slowly with increasing the methanol concentration in the mixture than it would be expected from the increase in viscosity of the solvent mixtures in the water-rich region. The constancy of the Walden product also fails in general for small ions in mixed solvents.<sup>19</sup>

In Fig. 4, the dependences of the thermodynamic dissociation constant  $PK_a$  of SA on the inverse dielectric constant of solutions calculated by the Hsia–Fuoss and

**Table 2.** Conductance parameters of salicylic acid in methanol–water mixtures at 25 °C calculated using the Hsia–Fuoss (in numerator) and Fuoss-78 (in denominator) equations

$\alpha$	$\lambda_0$ /S cm <sup>2</sup> mol <sup>-1</sup>	$K_A \cdot 10^{-3}$ /dm <sup>3</sup> mol <sup>-1</sup>	$\sigma$ (%)	$R/\text{Å}$
0	<u>385.60±0.02</u>	<u>0.985±0.001</u>	<u>0.026</u>	<u>3.57</u>
	386.06±0.04	1.004±0.001	0.024	3.57
19.79	<u>249.89±0.01</u>	<u>1.676±0.003</u>	<u>0.022</u>	<u>4.01</u>
	249.99±0.02	1.699±0.002	0.002	4.01
37.54	<u>170.00±0.01</u>	<u>3.963±0.009</u>	<u>0.038</u>	<u>4.56</u>
	170.03±0.01	4.000±0.005	0.022	4.56
49.97	<u>150.16±0.01</u>	<u>5.966±0.009</u>	<u>0.068</u>	<u>5.02</u>
	150.16±0.02	6.013±0.006	0.054	5.02
72.55	<u>106.87±0.01</u>	<u>19.735±0.071</u>	<u>0.080</u>	<u>6.43</u>
	105.45±0.01	19.126±0.007	0.042	6.43
90.59	<u>71.05±0.01</u>	<u>925.222±1.754</u>	<u>0.087</u>	<u>7.65</u>
	70.29±0.01	900.897±0.215	0.076	7.65

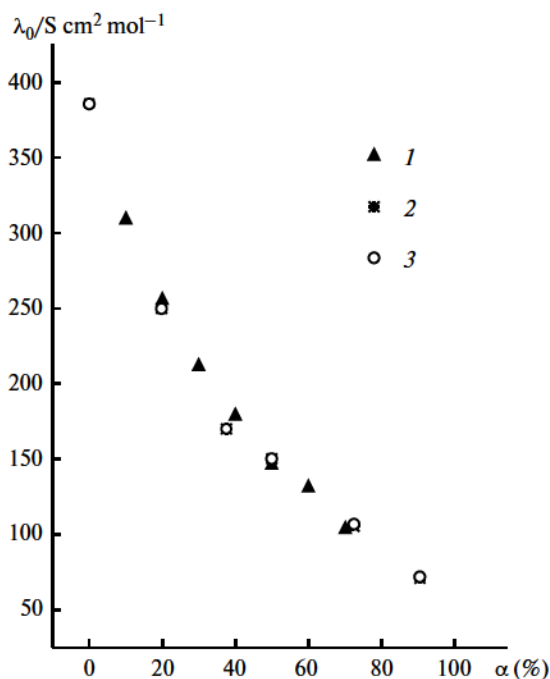


Fig. 1. Limiting equivalent conductance ( $\lambda_0$ ) plotted vs. methanol content ( $\alpha$ ) in methanol–water mixtures: published data<sup>6</sup> (1) and results of calculations by the Fuoss-78 (2) and Hsia–Fuoss (3) methods.

Fuoss-78 methods are compared with the values obtained using the Lee–Wheaton conductance equation.<sup>6</sup> Similar

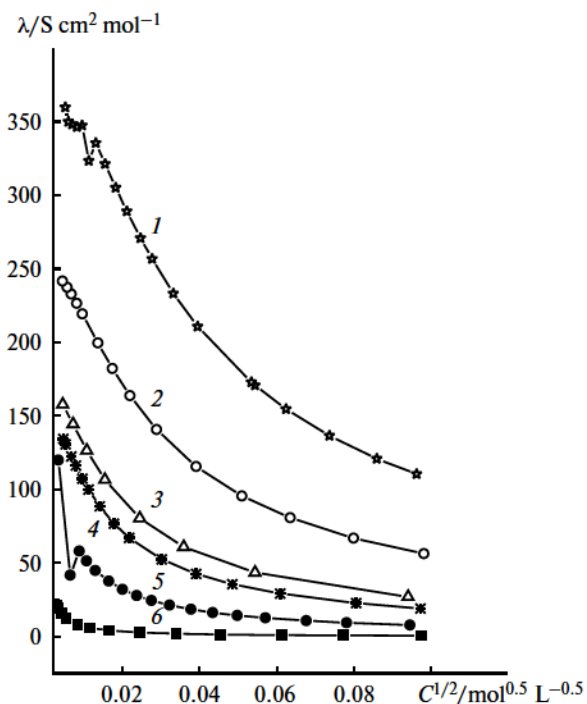


Fig. 2. Molar conductance plotted vs. solvent mixture compositions at 25 °C:  $\alpha = 0$  (1), 19.79 (2), 37.54 (3), 49.97 (4), 72.55 (5), and 90.59% (6).

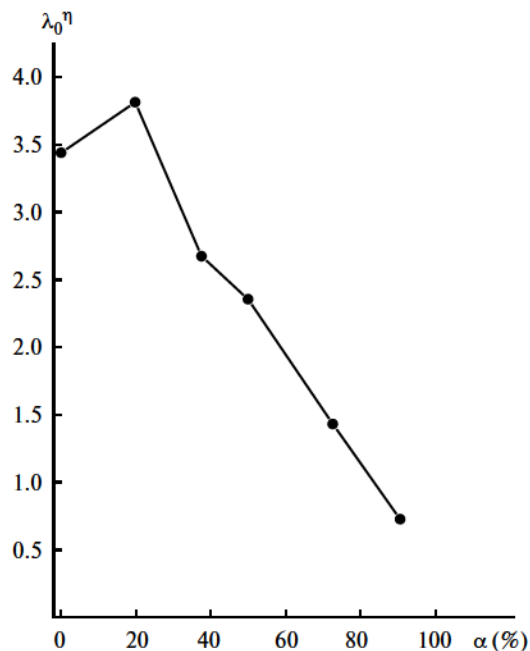


Fig. 3. Walden product plotted vs. solvent mixture composition.

variations were also found for SA in water mixtures with ethanol,<sup>5</sup> 1-propanol,<sup>8</sup> and acetone.<sup>6</sup> The  $PK_a$  values in aqueous solutions calculated by the two methods are in excellent agreement with those found by other methods of analysis.<sup>4,7–9</sup> Increased association upon adding methanol was explained by stabilization of anion owing to formation of an internal hydrogen bond between the carboxyl and hydroxyl groups.<sup>4,7,8</sup>

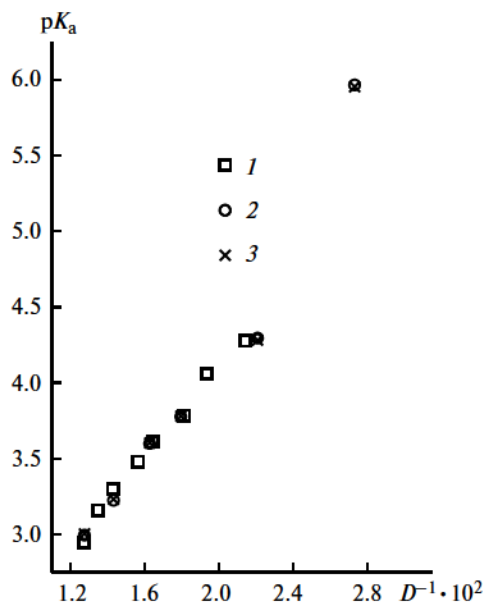


Fig. 4.  $PK_a$  values plotted vs. inverse dielectric constant of solution: results of calculations carried out using the Lee–Wheaton conductance equation<sup>6</sup> (1) and by the Hsia–Fuoss (2) and Fuoss-78 (3) methods.

Summing up, the conductivity of SA in methanol–water mixtures was measured at 25 °C and the results obtained were analyzed by the Hsia–Fuoss and Fuoss–78 methods. It was found that the limiting conductances and association constants differ slightly from those obtained by other methods of analysis. The  $\lambda_0$  values determined by the Hsia–Fuoss, Fuoss–78, and Lee–Wheaton<sup>6</sup> methods vary with the concentration of methanol in the mixtures in the same way. This confirms the validity of application of the former two methods. The  $\lambda_0$  value changes as the solvent composition changes, thus indicating rather strong ion–solvent interactions.<sup>20–25</sup>

It seems necessary to study the temperature dependence of conductivity to get more information on the behavior of SA in binary mixtures.

The lack of transference data in the literature precludes detailed interpretation of the concentration dependence of conductance.

### References

1. E. Grunwald, B. J. Berkowitz, *J. Am. Chem. Soc.*, 1951, **73**, 4939.
2. K. T. Novrk, K. J. Box, A. Avdeef, *Int. J. Pharm.*, 1997, **151**, 235.
3. G. Völgyi, R. Ruiz, K. Box, J. Comer, E. Bosch, K. T. Novák, *Anal. Chim. Acta.*, 2007, **583**, 418.
4. L. G. Bray, J. F. J. Dippy, S. R. Hughes, L. W. Laxton, *J. Chem. Soc.*, 1957, 2405.
5. A. K. Mandal, S. C. Lahiri, *Bull. Chem. Soc. Jpn*, 1976, **49**, 1829.
6. M. S. K. Niazi, S. S. Shah, M. Z. I. Khan, *J. Chem. Eng. Data*, 1993, **38**, 288.
7. J. F. J. Dippy, S. R. C. Hughes, B. C. Kitchiner, *J. Chem. Soc.*, 1964, 1275.
8. N. Papadopoulos, A. Avarans, *J. Solution. Chem.*, 1991, **20**, 293.
9. M. S. K. Niazi, M. Z. I. Khan, *J. Solution. Chem.*, 1993, **22**, 437.
10. Y. Xue, S. J. Traina, *Environ. Sci. Technol.*, 1996, **30**, 3177.
11. R. M. Fuoss, K. L. Hsia, *Proc. Natl. Acad. Sci.*, 1967, **57**, 1550.
12. R. M. Fuoss, *J. Phys. Chem.*, 1978, **82**, 2427.
13. K. Agnieszka, E. Hawlicka, *Phys. Chem. Chem. Phys.*, 2003, **5**, 4858.
14. R. F. Prini, *Trans. Faraday. Soc.*, 1969, **65**, 3311.
15. J. C. Justice, *Electrochim. Acta*, 1971, **16**, 701.
16. T. L. Broadwater, R. L. Kay, *J. Phys. Chem.*, 1970, **74**, 3802.
17. R. L. Kay, T. L. Broadwater, *Electrochim. Acta.*, 1971, **16**, 667.
18. R. L. Kay, T. L. Broadwater, *J. Solution. Chem.*, 1976, **5**, 57.
19. J. F. Skinner, R. M. Fuoss, *J. Phys. Chem.*, 1966, **70**, 1426.
20. R. M. Fuoss, *Proc. Nat. Acad. Sci.*, 1959, **45**, 807.
21. A. D'Aprano, R. M. Fuoss, *J. Phys. Chem.*, 1963, **67**, 1722.
22. R. Zwanzig, *J. Chem. Phys.*, 1963, **38**, 1603.
23. R. Zwanzig, *J. Chem. Phys.*, 1970, **52**, 3625.
24. P. Hemms, *J. Phys. Chem.*, 1974, **78**, 907.
25. A. D'Aprano, R. M. Fuoss, *J. Solution. Chem.*, 1975, **4**, 175.

Received June 26, 2012