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Application of the *ab initio* Theory and PCM–UAHF Model for Prediction of the pK_a for Formic and Silanoic Acids Derivatives in Aqueous Solution

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Ab initio molecular orbital methods at the CBSEQ level of theory have been used to study the structure and acidity of formic and silanoic acids derivatives in aqueous solution. The calculations are performed at the SCF level with inclusion of SCF–level thermochemical corrections to yield free energies of dissociation, using the basis sets 6- 31G** and the recently parametrized continuum–solvation method PCM–UAHF for the solvation contribution. The model furnishes pK_a values in relatively good agreement with experimental data. Scaling different parts of solvation energies provides a significant improvement in results and signifies the importance of balance of individual contributions from electrostatic, cavity, dispersion and repulsion interactions. The result shows that the investigated acids are weak and for C-acids the acidity increases in the order: CCl_3COOH > FCOOH > $CHCl_2COOH$ > $CH_2ClCOOH$ > HCOOH > NO_2COOH > CH_3COOH > NH_2COOH > BrCOOH > ClCOOH; their Si-acidity order is: CCl_3SiOOH > $CHCl_2SiOOH$ > FSiOOH > ClSiOOH > HSiOOH > BrSiOOH > $CH_2ClSiOOH$ > CH_3SiOOH > NO_2SiOOH > NH_2SiOOH.

Key Words: pK_a, Acidity, Formic acids, Silanoic acid, Solvation energy, Polarized continuum model, *Ab initio* calculations.

INTRODUCTION

Quantitative structure–property relationships are mathematical equations relating chemical, biological and technological properties. QSPR models, once established, can be used to predict properties of compounds as yet unmeasured or even unknown. Thus, QSPR approach saves resources and expedites the process of development of new molecules[1,2]. The acid-base properties of organic molecules affect their toxicity[3], chromatographic retention behaviour[4] and pharmaceutical properties[5]. In addition the acidity constants play a fundamental role in many analytical procedures such as acid base titration, solvent extraction, complex formation and ion transport. Therefore, having the knowledge about acid–base properties of chemical substances gives an idea about their toxicity, pharmaceutical activity and analytical roles. Much of the theoretical foundation of modern physical organic chemistry is based on the observation of the effects on acid–base equilibrium of changing molecular structure[6]. Proton transfer reactions constitute an important class of chemical reactions and have been studied extensively over a long period of time[7]. These studies in a gas phase and solution phase provides information on inherent substitute effects and solute–solvent interactions. The study of acidities in the gas phase allows assessment of effects in the absence of the perturbing influence of solvent or counter ions[8-10]. The acidity of compounds in solution phase is also of interest since many reactions occur practically and experimentally in solution phase. Many biological systems use proton–transfer reactions to perform communication between the extra cellular and intracellular media and the rate of these reactions depends on the degree of dissociation of the species[11].

For much smaller and congeneric series of compounds, solution–phase pK_a has also been correlated with gas–phase quantum chemical parameters[12,13] and for 135 organic oxy acids a method for predicting dissociation constants was developed on the basis of empirically calculated atomic charges[14]. Previous investigations of the more fundamental approach of applying quantum chemical continuum–solvation methods[15.16] for predicting solution–phase pK_a cover both semi empirical[17-19] and *ab initio* treatments[20,21]. The latter, however, were used only for a few compounds of small molecular size. As an overall result, acceptable correlations with relative pK_a trends were found within congeneric series of compounds, although the computational level was not sufficient to predict absolute pK_a values. Despite the gas–phase acidities, the calculations of acidities in solution phase are still deficient. This deficiency is due to the lack of a complete and precise model of solvation. Even recent models of solvation such as polarizable continuum model (PCM)[22] ignore some parts of solute–solvent interactions[23].

EXPERIMENTAL

The dissociation of an acid AH in aqueous solution[24],

$$AH_{aq} + H_2O_{aq} \rightleftharpoons A^-_{aq} + H_3O^+_{aq} \tag{1}$$

is governed by the equilibrium constant K, which is related to the dissociation constant K_a according to

$$K = \frac{[A^-_{aq}][H_3O^+]}{[AH_{aq}][H_2O_{aq}]} = \frac{K_a}{[H_2O_{aq}]} \tag{2}$$

(It is assumed that concentrations can be used instead of the activities).

The associated free energy change ΔG can be written for 1 M solutions at 298 K as

$$\Delta G_{(kcal/mol)} = -2.3RT \log K = 1.39\ pK_a + 2.36 \qquad (3)$$

and correspondingly, the solution-phase dissociation constant pK_a is given by

$$pK_a = 0.735\ \Delta G - 1.735 \qquad (4)$$

where ΔG is the standard change in the Gibbs free energy for the process in water at 298.15 K.

$$\begin{array}{l} HA_g + CH_3COO^-_g \xrightarrow{\Delta G^0_{gas}} A^-_g + CH_3COOH_g \\ \downarrow \Delta G^0_{HA,sol} \ \downarrow \Delta G^0_{CH_3COO^-,sol} \ \downarrow \Delta G^0_{A^-,sol} \ \downarrow \Delta G^0_{CH_3COOH,sol} \\ HA_{aq} + CH_3COO^-_{aq} \xrightarrow{\Delta G^0_2} A^-_{aq} + CH_3COOH_{aq} \end{array}$$

Scheme-I. The thermodynamic cycle proposed to convert ΔG^0_{gas} to ΔG

In order to calculate ΔG, we have used the thermodynamic cycle proposed by Namazian *et al.*[25], an isodesmic reaction, reaction (5) and the dissociation of acetic acid reaction (6) as reference molecule.

$$HA_{aq} + CH_3COO^-_{aq} \longrightarrow A^-_{aq} + CH_3COOH_{aq} \qquad (5)$$

$$CH_3COOH_{aq} + H_2O_{aq} \longrightarrow CH_3COO^-_{aq} + H_3O^+_{aq} \qquad (6)$$

The Gibbs energy of reaction (1), ΔG can be written as a sum of Gibbs energy of reaction (5), ΔG_1 and Gibbs energy of reaction (6), ΔG_2.

$$\Delta G = \Delta G_1 + \Delta G_2 \qquad (7)$$

Scheme-I shows a thermodynamic cycle proposed to calculate the ΔG_1. From this cycle, ΔG_1 is given by following expression

$$\Delta G_1 = \Delta G_{1,gas} + \Delta G_{1,sol} \qquad (8)$$

in which ΔG_1, sol is defined as follow:

$$\Delta G_{1,sol} = \Delta G_{A^-,sol} + \Delta G_{CH_3COOH,sol} - \Delta G_{HA,sol} - \Delta G_{CH_3COO^-_{sol}} \qquad (9)$$

The fourth term on the right-hand side of eqn. 9 represent free energies of solvation and have been computed with the recently developed *ab initio* continuum.solvation model PCM.UAHF[26]. For the free energy of proton transfer in the gas phase, ΔG, computational models with high accuracy like the G2 model[27,28] and complete basis set (CBS)[29] approaches would be typical methods of choice. For practical reasons, however, the following simplified approach was selected. The *ab initio* calculations have been performed at the level of Hartree-Fock. The zero-point energies and thermal corrections together with entropies have been used to convert the internal energies to the Gibbs energies at 298.15 K. A medium-size basis set, 6-31(d,p), has been chosen by considering the size of studied molecules. Higher level of theory was not justified because of hardware limitations and the significant length of time of computations. GAUSSIAN 98[30] have been employed for all *ab initio* calculations.

RESULTS AND DISCUSSION

The aim of present work is to provide a consistent and reliable set of gas phase and solvation phase acidities for C– and Si– acids R–MOOH [M = C, Si, R = H, F, Cl, Br, CH_3, CH_2Cl, $CHCl_2$, CCl_3, NH_2, NO_2] using at the Hartree Fock level of theory and 6-31(d, p) basis set and solvation energies obtained by PCM model. The calculated gas-phase energy and solvation energy of each acid and its corresponding anion together with the change of total standard Gibbs energy of reaction ($HA \rightarrow A^- + H^+$) is shown in Table-1. The change of Gibbs energy of deprotonation might be of theoretical interest, but only the differences between the most stable species can have physical meaning and can be compared with experiments. The

TABLE-1
GIBBS FREE ENERGY OF EACH MOLECULE AND ITS ANION IN THE GAS AND AQUEOUS PHASE TOGETHER WITH CHANGE OF GIBBS ENERGY, ΔG_{gas}, ΔG_{sol} IN THE GAS PHASE AND SOLVATION PHASE

Compdound	ΔG_{gas} (a.u.)		ΔG_{sol} (a.u.)		ΔG_{gas}	ΔG_{sol}
	Acid	Anion	Acid	Anion	kcal/mol	
HSiOOH	-439.84080	-439.28837	-440.14956	-439.67834	346.655	295.665
FSiOOH	-538.77351	-538.23304	-538.81839	-538.34830	339.144	298.450
ClSiOOH	-898.80610	-898.27737	-898.36770	-898.36770	331.783	295.959
BrSiOOH	-3009.22032	-3008.69082	-3008.77643	-3008.77643	332.266	295.933
CH_3SiOOH	-478.86930	-478.31303	-478.93240	-478.45710	349.065	304.430
$CH_2ClSiOOH$	-937.77260	-937.22801	-937.82705	-937.35281	341.735	301.230
$CHCl_2SiOOH$	-1396.66901	-1396.13687	-1396.70038	-1396.23149	333.917	294.227
CCl_3SiOOH	-1855.55301	-1855.03431	-1855.57710	-1855.11146	325.483	292.168
NH_2SiOOH	-494.90810	-494.34850	-494.96745	-494.48551	351.154	304.875
NO_2SiOOH	-643.37200	-642.81061	-643.40132	-642.92512	352.278	304.466
HCOOH	-188.74838	-188.18564	-188.77463	-188.30557	353.125	294.340
FCOOH	-287.63155	-287.09544	-287.65018	-287.19790	336.414	283.807
ClCOOH	-647.66465	-647.18621	-647.66515	-647.17069	300.226	310.275
BrCOOH	-2758.07280	-2757.60010	-2758.06753	-2757.58340	296.624	303.796
CH_3COOH	-227.76917	-227.20573	-227.82690	-227.35240	353.564	297.751
$CH_2ClCOOH$	-686.67704	-686.12970	-686.71842	-686.25583	343.461	290.282
$CHCl_2COOH$	-1145.57300	-1145.04120	-1145.60109	-1145.14620	333.710	285.448
CCl_3COOH	-1604.45960	-1603.94080	-1604.47321	-1604.02100	325.552	283.766
NH_2COOH	-243.79162	-243.22739	-243.84899	-243.37217	354.060	299.210
NO_2COOH	-392.21164	-391.72286	-392.26231	-391.79071	306.714	295.931

result shows that the acidities of acids in solvation phase is stronger than gas-phase. For C-acids studied CCl_3COOH and for Si-acids studied CCl_3SiOOH is strongest acid.

Using the total Gibbs free energies, the pK_a values have been calculated using eqn. 4 and the results are shown in Table-2, where they are compared with those obtained from the experimental values. Inspection of calculated pK_a reveals that in most cases the pK_a values are reasonably close to the experimental values. For example, the calculated pK_a are 3.75 and 4.73 for formic acid and acetic acid, respectively whereas the experimental pK_a is reported to be 3.75 and 4.76. The data distribution of calculated values *vs.* experimental data for pK_a is shown in Fig. 1. In the some cases, large deviations are observed. These deviations are mainly because of solvation energies and they are for polar substituent such as halogen groups. The pK_a values are in the range of 0.74 for CCl_3COOH to 6.06 for NH_2SiOOH. The experimental acidities of silanoic acid and its derivatives are not known. Therefore, it is not possible to compare the present theoretical results directly with experiments.

TABLE-2
GAS-PHASE AND SOLVATION ENERGIES AND pK_a VALUES CALCULATED IN THIS WORK USING PCM MODEL

Compound	ΔG_{1gas} (kcal/mol)	ΔG_{1sol} (kcal/mol)	$pK_{a,cal}$	$pK_{a,exp}$[a]
HCOOH	-0.001	-0.005	3.75	3.75
FCOOH	-0.027	0.005	0.75	
ClCOOH	-0.085	0.105	8.30	
BrCOOH	-0.091	0.100	6.45	
CH_3COOH	0.000	0.000	4.73	4.76
$CH_2ClCOOH$	-0.016	0.004	2.59	2.86
$CHCl_2COOH$	-0.032	0.012	1.22	1.30
CCl_3COOH	-0.045	0.022	0.74	
NH_2COOH	0.001	0.002	5.14	
NO_2COOH	-0.075	0.072	4.20	
HSiOOH	-0.011	0.008	4.14	
FSiOOH	-0.023	0.019	3.94	
ClSiOOH	-0.035	0.031	4.04	
BrSiOOH	-0.034	0.031	4.23	
CH_3SiOOH	-0.007	0.008	4.87	
$CH_2ClSiOOH$	-0.019	0.019	4.68	
$CHCl_2SiOOH$	-0.031	0.026	3.73	
CCl_3SiOOH	-0.044	0.036	3.14	
NH_2SiOOH	-0.004	0.011	6.06	
NO_2SiOOH	-0.002	0.004	5.04	

[a] The experimental values are taken from Ref. 24.

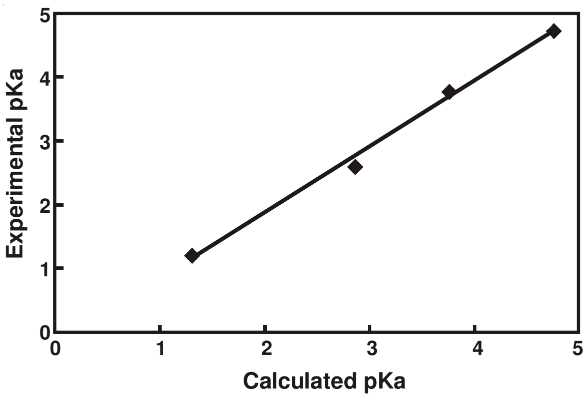

Fig. 1.

TABLE-3
SOLVATION ENERGY AND ITS FOUR COMPONENTS (ELECTROSTATIC INTERACTION, CAVITY TERM AND DISPERSION AND REPULSION ENERGIES) OF EACH MOLECULE AND ITS CORRESPONDING ANION CALCULATED USING DPCM MODEL (ALL VALUES ARE IN kcal/mol)

Compound	ΔG_{ele}		ΔG_{cav}		ΔG_{dis}		ΔG_{rep}		ΔG_{solv}	
	Acid	Anion	Acid	Anion	Acid	Anion	Acid	Anion	Acid	Anion
HCOOH	-13.89	-76.81	7.64	6.66	-8.31	-8.12	1.88	2.08	-12.68	-76.19
FCOOH	-10.77	-71.60	8.62	7.77	-9.09	-9.16	1.79	2.18	-9.45	-70.81
ClCOOH	-9.70	-72.35	10.35	11.15	-10.15	-10.47	1.60	2.17	-7.90	-69.49
BrCOOH	-8.65	-68.78	11.03	11.59	-10.87	-11.55	1.67	2.39	-6.81	-66.34
CH_3COOH	-12.24	-77.59	9.95	9.11	-10.79	-10.91	2.06	2.50	-11.01	-76.89
$CH_2ClCOOH$	-10.03	-71.46	12.27	11.60	-13.01	-13.41	2.37	305	-8.40	-70.22
$CHCl_2COOH$	-9.95	-67.68	14.98	14.39	-14.23	-14.65	2.40	2.99	-6.81	-64.95
CCl_3COOH	-8.29	-61.40	17.17	16.70	-15.09	-15.42	1.79	2.29	-4.43	-57.83
NH_2COOH	-18.85	-81.06	9.10	8.28	-11.05	-11.13	2.67	3.08	-18.13	-80.83
NO_2COOH	-10.24	-58.97	11.72	11.66	-11.24	-11.89	1.66	2.37	-8.09	-56.84
HSiOOH	-40.17	-0.55	7.89	7.35	-9.48	-9.64	13.38	19.30	-28.37	-16.46
FSiOOH	-35.06	-83.17	10.02	9.58	-7.54	-6.85	1.76	1.52	-30.82	-78.92
ClSiOOH	-29.08	-72.26	11.82	11.38	-8.83	-8.33	1.67	1.52	-24.42	-67.69
BrSiOOH	-27.11	-70.74	12.38	11.91	-9.64	-9.24	1.74	1.64	-22.62	-66.42
CH_3SiOOH	-24.78	-78.14	11.75	11.22	-9.04	-8.59	1.82	1.75	-20.25	-73.76
$CH_2ClSiOOH$	-26.65	-75.07	13.96	13.69	-11.46	-11.31	2.11	2.36	-22.05	-70.32
$CHCl_2SiOOH$	-21.56	-68.81	16.83	16.68	-13.10	-12.86	2.37	2.46	-15.45	-62.54
CCl_3SiOOH	-25.66	-66.71	19.76	19.19	-14.20	-13.84	1.93	1.86	-18.17	-59.49
NH_2SiOOH	-32.69	-83.08	10.58	10.14	-9.61	-8.99	2.73	2.67	-28.99	-79.26
NO_2SiOOH	-31.78	-73.74	13.37	13.33	-10.68	-9.38	2.21	1.67	-26.89	-68.11

Different solvation algorithms have been employed in order to calculate solvation energies. These models have been Dielectric-CPCM (DPCM)[31], Conductor-CPCM (CPCM)[32] and Integral equation Formalism-

CPCM (IEFPCM)[33]. These methods are different in their modeling of the cavity created in solvent in order to place the solute molecules. The isodensity surface, which is employed in the recent version of PCM methods, is a natural shape for the cavity and it corresponds to the reactive shape of molecules. The solvation energy of each molecule and its anion calculated using DPCM, CPCM and IEFPCM models are shown in Tables 3-5 as well as four components of solvation energies from the electrostatic interaction, cavity term, dispersion and repulsion energies. Examination of the calculated values shows that electrostatic interactions between anions and solvent are much greater than interaction of neutral molecules and solvent (seven to ten times for formic acid derivatives and two to three times for silanoic acids derivatives). Dispersion and repulsion energies of anions are also greater than acids because of the extra net charge on anions. Cavity energies of acids are slightly greater than anions because of the extra hydrogen atom. The overall calculated solvation energies of anions are of significant and play an important role in total solvation energy of reaction (5).

TABLE-4
SOLVATION ENERGY AND ITS FOUR COMPONENTS (ELECTROSTATIC INTERACTION, CAVITY TERM AND DISPERSION AND REPULSION ENERGIES) OF EACH MOLECULE AND ITS CORRESPONDING ANION CALCULATED USING CPCM MODEL (ALL VALUES ARE IN kcal/mol)

Compound	ΔG_{ele}		ΔG_{cav}		ΔG_{dis}		ΔG_{rep}		ΔG_{solv}	
	Acid	Anion	Acid	Anion	Acid	Anion	Acid	Anion	Acid	Anion
HCOOH	-13.89	-76.81	7.64	6.66	-8.31	-8.12	1.88	2.08	-12.68	-76.19
FCOOH	-10.77	-71.60	8.62	7.77	-9.09	-9.16	1.79	2.18	-9.45	-70.81
ClCOOH	-9.70	-72.35	10.35	11.15	-10.15	-10.47	1.60	2.17	-7.90	-69.49
BrCOOH	-8.65	-68.78	11.03	11.59	-10.87	-11.55	1.67	2.39	-6.81	-66.34
CH_3COOH	-12.24	-77.59	9.95	9.11	-10.79	-10.91	2.06	2.50	-11.01	-76.89
$CH_2ClCOOH$	-10.03	-71.46	12.27	11.60	-13.01	-13.41	2.37	305	-8.40	-70.22
$CHCl_2COOH$	-9.95	-67.68	14.98	14.39	-14.23	-14.65	2.40	2.99	-6.81	-64.95
CCl_3COOH	-8.29	-61.40	17.17	16.70	-15.09	-15.42	1.79	2.29	-4.43	-57.83
NH_2COOH	-18.85	-81.06	9.10	8.28	-11.05	-11.13	2.67	3.08	-18.13	-80.83
NO_2COOH	-10.24	-58.97	11.72	11.66	-11.24	-11.89	1.66	2.37	-8.09	-56.84
HSiOOH	-17.29	-75.54	7.89	7.35	-9.48	-9.64	13.38	19.30	-16.50	-58.53
FSiOOH	-37.58	-84.81	10.02	9.58	-7.54	-6.85	1.76	1.52	-33.35	-80.56
ClSiOOH	-30.95	-73.71	11.82	11.38	-8.83	-8.33	1.67	1.52	-26.29	-69.13
BrSiOOH	-29.90	-72.52	12.38	11.91	-9.64	-9.24	1.74	1.64	-25.42	-68.21
CH_3SiOOH	-26.73	-77.29	11.75	13.69	-9.04	-11.31	1.82	2.36	-22.20	-72.54
$CH_2ClSiOOH$	-30.15	-77.25	13.96	13.69	-11.46	-11.31	2.11	2.36	-25.55	-72.51
$CHCl_2SiOOH$	-30.16	-71.77	16.83	16.68	-13.10	-12.86	2.37	2.46	-24.06	-65.49
CCl_3SiOOH	-31.91	-72.52	19.76	11.91	-14.20	-9.24	1.93	1.64	-24.42	-68.21
NH_2SiOOH	-34.43	-86.06	10.58	10.14	-9.61	-8.99	2.73	2.67	-30.73	-82.24
NO_2SiOOH	-36.13	-79.32	13.37	13.33	-10.68	-9.38	2.21	1.67	-31.24	-73.69

TABLE-5
SOLVATION ENERGY AND ITS FOUR COMPONENTS (ELECTROSTATIC INTERACTION, CAVITY TERM AND DISPERSION AND REPULSION ENERGIES) OF EACH MOLECULE AND ITS CORRESPONDING ANION CALCULATED USING IEFCPCM MODEL (ALL VALUES ARE IN kcal/mol)

Compound	ΔG_{ele}		ΔG_{cav}		ΔG_{dis}		ΔG_{rep}		ΔG_{solv}	
	Acid	Anion	Acid	Anion	Acid	Anion	Acid	Anion	Acid	Anion
HCOOH	-13.70	-75.42	7.64	6.66	-8.31	-8.12	1.88	2.08	-12.50	-74.80
FCOOH	-10.59	-70.69	8.62	7.77	-9.09	-9.16	1.79	2.18	-9.27	-69.90
ClCOOH	-9.24	-71.08	10.35	11.15	-10.15	-10.47	1.60	2.17	-7.44	-68.23
BrCOOH	-8.90	-67.84	11.03	11.59	-10.87	-11.55	1.67	2.39	-7.07	-65.39
CH_3COOH	-12.26	-76.38	9.95	9.11	-10.79	-10.91	2.06	2.50	-11.03	-75.68
$CH_2ClCOOH$	-10.17	-70.02	12.27	11.60	-13.01	-13.41	2.37	305	-8.54	-68.78
$CHCl_2COOH$	-11.56	-66.01	14.98	14.39	-14.23	-14.65	2.40	2.99	-8.41	-63.28
CCl_3COOH	-8.32	-60.19	17.17	16.70	-15.09	-15.42	1.79	2.29	-4.46	-56.62
NH_2COOH	-18.56	-79.89	9.10	8.28	-11.05	-11.13	2.67	3.08	-17.84	-79.66
NO_2COOH	-6.41	-58.18	11.72	11.66	-11.24	-11.89	1.66	2.37	-4.27	-56.04
HSiOOH	-17.07	-26.60	7.89	7.35	-9.48	-9.64	13.38	19.30	-16.27	-50.59
FSiOOH	-37.15	-83.73	10.02	9.58	-7.54	-6.85	1.76	1.52	-32.92	-79.47
ClSiOOH	-30.42	-72.81	11.82	11.38	-8.83	-8.33	1.67	1.52	-25.76	-68.23
BrSiOOH	-29.53	-71.77	12.38	11.91	-9.64	-9.24	1.74	1.64	-25.05	-67.45
CH_3SiOOH	-26.39	-76.31	11.75	13.69	-9.04	-11.31	1.82	2.36	-21.86	-71.56
$CH_2ClSiOOH$	-29.83	-76.31	13.96	13.69	-11.46	-11.31	2.11	2.36	-25.23	-71.56
$CHCl_2SiOOH$	-29.84	-70.95	16.83	16.68	-13.10	-12.86	2.37	2.46	-23.74	-64.68
CCl_3SiOOH	-31.40	-71.77	19.76	11.91	-14.20	-9.24	1.93	1.64	-23.91	-67.45
NH_2SiOOH	-34.11	-84.89	10.58	10.14	-9.61	-8.99	2.73	2.67	-30.41	-81.06
NO_2SiOOH	-35.74	-77.71	13.37	13.33	-10.68	-9.38	2.21	1.67	-30.85	-72.09

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