

SOLVENT EFFECTS ON DISSOCIATION OF SUBSTITUTED BENZENESULPHONAMIDES IN ACETONE, 1,2-DICHLOROETHANE, TETRAMETHYLENE SULPHONE, PYRIDINE AND SOME AQUEOUS ORGANIC SOLVENT MIXTURES*

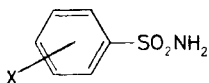
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The potentiometric titration has been used to measure dissociation constants of fifteen substituted arenesulphonamides of general formula $\text{XC}_6\text{H}_4\text{SO}_2\text{NH}_2$ (or $\text{X}_2\text{C}_6\text{H}_3\text{SO}_2\text{NH}_2$) in acetone, 1,2-dichloroethane, tetramethylene sulphone, pyridine, and mixtures water-ethanol (25, 50, 75, 90% by vol. of the organic component), water-dimethylformamide (25, 50, 75% by vol.), water-acetone (25% by vol.), and water-2-methoxyethanol (80% by wt.). The results are compared with those published earlier for water, methanol, ethanol, dimethylformamide, dimethyl sulphoxide, and acetonitrile.

The benzenesulphonamides of general formula I



were studied with regard to their acid-base properties in amphiprotic solvents – water^{1,2}, methanol¹, ethanol¹, and 50% (by wt.) ethanol³⁻⁵, in dipolar aprotic solvents – dimethyl sulphoxide⁶, dimethylformamide⁶, and acetonitrile⁶. In all the reports mentioned the Hammett substitution relation was evaluated. An attempt was made at quantitative description of solvent effects on the dissociation of the acids studied^{1,6}. Theoretical relations concerning the dissociation of weak acids in amphiprotic and aprotic solvents were discussed in our previous communications^{1,6}. The solvents dealt in the present communication (except 1,2-dichloroethane) fall into the following two groups: 1) amphiprotic – mixed solvents, 2) aprotic solvents – acetone, tetramethylene sulphone. Although 1,2-dichloroethane belongs to inert solvents, it possesses the highest relative permittivity in the group investigated.

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There exists a working acidity scale in this solvent^{7,8} which can be considered aprotic to a certain extent. Several difficulties⁹⁻¹² can be encountered with little polar solvents to which 1,2-dichloroethane belongs: 1) a smaller potential jump at the half neutralization point; 2) unsymmetrical plateau of the titration curve; 3) the potential jumps corresponding to simple fractions of the total neutralization. When these difficulties appear, the reproducibility of results is diminished.

The present communication deals with estimation of the dissociation constants of substituted benzenesulphonamides by potentiometric titration in acetone, pyridine, tetramethylene sulphone, 1,2-dichloroethane, and some mixtures of water-methanol, water-dimethylformamide, water-acetone, and water-methylcellosolve. Moreover, it describes the substituent effects in the solvents mentioned and compares the results with those already published^{1,6} about the dissociation of the acids studied.

EXPERIMENTAL

Syntheses of the model substances, titration agent, calibration buffer, and experimental conditions of the measurements were described in our previous communications^{1,6}.

Purification of Solvents

Acetone (Lachema, *p.a.*) was dried with anhydrous calcium chloride (150 g per 1 l solvent) for two days. After decantation and distillation it was left to stand with anhydrous calcium sulphate (Driethe, 400 g per 1 l solvent) and again decanted and distilled with exclusion of air humidity.

1,2-Dichloroethane (Reaktivul, *p.a.*) was repeatedly shaken with concentrated sulphuric acid (30 ml per 1 l solvent) until the acid layer remained colourless. Then the solvent was shaken with redistilled water until neutral, whereafter it was kept over anhydrous calcium chloride in a dark-coloured bottle. In the subsequent distillation, a fraction boiling in the range of 83 to 83.5°C was taken. From the solvent obtained, 100 ml was removed by distillation, and the residue was left to cool with exclusion of air humidity.

Dimethylformamide⁶ and methanol¹ were purified by the procedures given in literature.

2-Methoxyethanol (methylcellosolve) (UCB, *p.a.*) was kept over potassium hydroxide (200 g per 1 l solvent) 2 days. After decantation it was distilled twice through a column with exclusion of air humidity.

Tetramethylene sulphone (Merck, *p.a.*) was heated to 35°C and treated with activated alumina (150 g Al₂O₃ per 1 l solvent). The mixture was shaken 2 h while keeping the solvent in liquid state. Then the solvent was distilled in vacuum.

Pyridine (Avondale, *p.a.*) was shaken with powdered potassium hydroxide (150 g per 1 l solvent) and left to stand therewith several days with intermittent shaking. Then the solvent was distilled, and the middle fraction (80%) was taken.

Potentiometric Measurements

The dissociation constants were determined by potentiometric titration using an RTS-622 apparatus (Radiometer) and a hydrated glass electrode whose hydration with 0.1 mol l⁻¹ hydrochloric acid was repeated whenever its response was slowed down. When not in operation, the electrode was immersed in an aqueous buffer of pH 7.00. The reference electrode was a calomel electrode with saturated solution of potassium chloride in methanol.

The electrodes system was calibrated with the use of the following pK_{HA} values of the calibration buffers in the given organic solvents: 1,2-dichloroethane (picric acid 13.7, benzoic acid 20.0)¹², pyridine (2,4-dinitrophenol 4.38, 2,6-dinitrophenol 4.7, picric acid 3.5, benzoic acid 9.8)¹³⁻¹⁵, acetone (picric acid 9.2, benzoic acid 18.2)^{16,17}, tetramethylene sulphone (picric acid 17.4, benzoic acid 26.3)^{17,18}. For the calibration of electrodes in mixed solvents we used the linear section of the titration curve of benzoic acid in the given medium. The pK_{HA} values used for benzoic acid: water-methanol (25% — 4.60, 50% — 5.23, 75% — 6.00, 90% — 6.83)¹⁹, water-dimethylformamide (25% — 4.76, 50% — 5.25, 75% — 7.90)²⁰, water-acetone (25% — 4.92)^{21,22}, water-methylcellosolve (80% — 6.63)²³.

The titration procedure of sulphonamides (initial concentration of $5 \cdot 10^{-3} \text{ mol l}^{-1}$) was described in the previous communication¹.

RESULTS AND DISCUSSION

Tables I–IV present the pK_{HA} dissociation constants of benzenesulphonamides measured by the potentiometric titration in acetone, pyridine, 1,2-dichloroethane, tetramethylene sulphone, and mixtures water-methanol, water-dimethylformamide, water-acetone, water-methylcellosolve. Table V gives the parameters of the Hammett equation calculated from all the repeated measurements in a given solvent (the table gives the values including the results obtained for the solvents in the previous communications^{1,6}).

If the solvents are arranged according to the increasing pK_{HA}^0 values (pK_{HA}^0 means the pK_{HA} value of the parent unsubstituted substrate calculated from the Hammett equation) the following order is obtained: water (9.43) < pyridine (13.74) < methanol (14.39) < dimethyl sulphoxide (15.24) < ethanol (15.77) < dimethylformamide (17.00) < acetone (24.51) \cong acetonitrile (24.52) < 1,2-dichloroethane (25.08) < tetramethylene sulphone (31.91). Comparison of the pK_{HA} values, which represent a measure of acidity in the individual media, is complicated by the fact that no absolute scale is available. By transition to the standard acidity scale⁷ a certain standard state is established in each solvent which is characterized by the value of standard potential of the silver chloride electrode (${}_sE^0$). This transition adjusts the beginnings of the acidity scales in the individual media at the same level, and from this moment we always only compare the potential measured with the standard potential. This shift of scale, at the same time, removes the effect of solvent on the beginning of the scale, the theoretical slope of the dependence between mV and pH (59.16 mV per one pH unit) being maintained for all the media. The transition from the standard to the conventional⁷ and working⁷ acidity scale does not cause any more shifts of the scales in the individual solvents. Hence a comparison of the pK_{HA} values determined in the working pH scales in the individual solvents in fact means the comparison of differences between the potentials in the half neutralization point and in the standard state in various media. It is important that the beginning of the scales was determined in the same way for all the solvents. Hence the pK_{HA} values of the substrate in various media only represent a measure of the solvent

TABLE I

The values of dissociation constants (in the form of pK_{HA}) of sulphonamides $XC_6H_4SO_2NH_2$ or $X_2C_6H_3SO_2NH_2$ measured in pyridine, 1,2-dichloroethane and tetramethylene sulphone

X	pK_{HA}					
	pyridine		1,2-dichloroethane		tetramethylene sulphone	
H	13·75	13·67	24·91	24·98	31·89	32·04
	13·79	13·66	25·07	24·98	32·04	31·80
4-CH ₃	13·84	14·06	25·47	25·14	32·22	32·34
	14·09	14·08	25·33	25·20	32·26	32·16
3-CH ₃	14·25	13·87	25·21	25·14	32·11	32·19
	13·93	13·81	25·39	25·13	32·31	32·11
3,4-(CH ₃) ₂	14·25	14·31	25·41	25·52	32·44	32·43
	14·43	14·27	25·52	25·57	32·66	32·33
4-Cl	13·14	13·01	24·55	24·59	31·26	31·27
	13·14	13·36	24·65	24·79	31·40	31·11
3-Cl	13·00	13·01	24·42	24·39	31·02	31·05
	12·89	13·18	24·37	24·18	31·09	31·01
3,4-Cl ₂	12·25	12·56	24·03	24·20	30·46	30·50
	12·62	12·71	24·11	24·11	30·58	30·50
4-NO ₂	12·20	12·15	23·56	23·96	30·22	30·33
	12·30	12·22	23·75	23·72	30·38	30·19
3-NO ₂	11·98	12·20	23·88	23·83	30·29	30·43
	12·34	12·30	23·67	23·88	30·45	30·29
3-OCH ₃	13·72	13·63	25·02	24·88	31·82	31·92
	13·74	13·57	25·36	25·03	32·07	31·87
4-OCH ₃	14·33	14·09	25·55	25·48	32·50	32·51
	14·36	14·25	25·66	25·57	32·60	32·28
4-Br	13·36	13·26	24·77	24·59	31·28	31·43
	13·06	13·43	24·76	24·79	31·42	31·38
4-F	13·55	13·26	24·64	24·67	31·55	31·60
	13·35	13·32	24·89	24·87	31·63	31·51
4-CF ₃	12·65	12·73	24·09	23·37	30·65	30·75
	12·82	12·91	24·23	24·11	30·87	30·68
3-CN	12·30	12·41	23·86	24·03	30·55	30·57
	12·47	12·47	23·74	24·25	30·66	30·58

TABLE II

The values of dissociation constants (in the form of pK_{HA}) of sulphonamides $XC_6H_4SO_2NH_2$ or $X_2C_6H_3SO_2NH_2$ measured in 25%, 50%, 75% (by vol.) dimethylformamide-water mixtures

X	pK_{HA}					
	25% dimethylformamide		50% dimethylformamide		75% dimethylformamide	
H	10·27	10·24	10·87	10·92	12·10	12·08
	10·27	10·27	10·89	10·85	12·10	12·06
4-CH ₃	10·36	10·32	11·14	11·16	12·31	12·27
	10·40	10·39	11·02	11·11	12·27	12·30
3-CH ₃	10·34	10·24	10·99	10·95	12·16	12·15
	10·34	10·34	10·95	10·99	12·16	12·15
3,4-(CH ₃) ₂	10·42	10·44	11·15	11·22	12·38	12·40
	10·49	10·50	11·12	11·17	12·37	12·47
4-Cl	9·90	9·89	10·53	10·57	11·62	11·62
	9·95	9·92	10·50	10·53	11·59	11·59
3-Cl	9·75	9·81	10·35	10·43	11·45	11·37
	9·77	—	10·29	10·36	11·38	11·40
3,4-Cl ₂	9·51	9·54	10·01	10·14	11·00	10·94
	9·57	9·54	10·05	10·07	11·00	10·98
4-NO ₂	9·31	9·28	9·79	9·82	10·81	10·76
	9·30	9·31	9·80	9·81	10·74	10·71
3-NO ₂	9·32	9·29	9·83	9·89	10·87	10·84
	9·39	—	9·89	9·85	10·84	10·79
3-OCH ₃	10·12	10·10	10·83	10·87	12·00	11·94
	10·15	10·17	10·78	10·85	12·01	11·98
4-OCH ₃	10·39	10·44	11·12	11·17	12·40	12·37
	10·50	10·48	11·06	11·14	12·40	12·43
4-Br	9·98	9·98	10·49	10·48	11·62	11·57
	9·97	—	10·50	10·53	11·58	11·59
4-F	10·06	10·06	10·70	10·72	11·79	11·77
	10·08	10·11	10·65	10·68	11·72	11·79
3-CF ₃	9·67	9·64	10·23	10·26	11·28	11·18
	9·70	9·66	10·19	10·23	11·21	11·22
3-CN	9·43	9·49	9·99	10·02	11·05	10·96
	9·48	9·45	9·99	9·99	10·96	10·96

TABLE III

The values of dissociation constants (in the form of pK_{HA}) of sulphonamides $XC_6H_4SO_2NH_2$ or $X_2C_6H_3SO_2NH_2$ measured in 25%, 50%, 75%, and 90% (by vol.) methanol-water mixture

X	pK_{HA}							
	25% methanol		50% methanol		75% methanol		90% methanol	
H	9.64	9.64	10.16	10.18	10.77	10.73	11.39	11.35
	9.66	9.66	10.19	10.19	10.78	10.76	11.33	11.26
4-CH ₃	9.83	9.76	10.30	10.26	10.80	10.74	11.43	11.35
	9.80	9.78	10.35	10.27	10.83	10.83	11.36	11.33
3-CH ₂	9.72	9.74	10.28	10.24	10.72	10.70	11.40	11.34
	9.74	9.72	10.35	10.33	10.78	10.77	11.36	11.31
3,4-(CH ₃) ₂	9.89	9.90	10.36	10.45	10.82	10.81	11.49	11.36
	9.88	9.88	10.45	10.39	10.87	10.87	11.43	11.40
4-Cl	9.44	9.36	9.90	9.92	10.40	10.38	11.19	11.14
	9.37	9.37	9.97	9.95	10.45	10.45	11.14	11.06
3-Cl	9.25	9.19	9.79	9.77	10.32	10.32	11.06	11.03
	9.25	9.25	9.85	9.79	10.37	10.37	11.02	10.94
3,4-Cl ₂	9.01	9.03	9.58	9.58	10.03	10.10	10.83	10.79
	9.01	9.02	9.60	9.55	10.05	10.06	10.81	10.76
4-NO ₂	8.75	8.77	9.31	9.30	9.80	9.77	10.61	10.65
	8.77	8.78	9.34	9.41	9.85	9.85	10.57	10.57
3-NO ₂	8.83	8.83	9.37	9.37	9.84	9.91	10.61	10.67
	8.82	8.84	9.39	9.41	9.90	9.90	10.61	10.61
3-OCH ₃	9.60	9.59	10.11	10.13	10.64	10.60	11.34	11.32
	9.59	9.63	10.19	10.14	10.64	10.65	11.33	11.30
4-OCH ₃	9.90	9.85	10.31	10.32	10.78	10.81	11.49	11.37
	9.85	—	10.43	10.37	10.86	10.87	11.41	11.38
4-Br	—	—	9.86	9.86	10.36	10.41	11.14	11.13
	—	—	9.87	9.86	10.47	10.46	11.13	11.08
4-F	9.56	9.53	9.96	10.04	10.54	10.50	11.27	11.21
	9.52	9.52	10.10	10.05	10.53	10.53	11.20	11.18
3-CF ₃	9.12	9.14	9.63	9.63	10.12	10.19	10.95	10.92
	9.14	9.12	9.71	9.63	10.18	10.15	10.92	10.90
3-CN	8.92	8.90	9.45	9.42	9.99	10.06	10.80	10.76
	8.91	8.88	9.49	9.41	10.01	10.02	10.72	10.69

TABLE IV

The values of dissociation constants (in the form of pK_{HA}) of sulphonamides $XC_6H_4SO_2NH_2$ or $X_2C_6H_3SO_2NH_2$ measured in neat acetone and in mixtures 25% (by vol.) acetone-water and 80% (by wt.) methylcellosolve-water

X	pK_{HA}					
	acetone		25% acetone		80% methylcellosolve	
H	24.53	24.73	8.46	8.40	11.95	11.90
	24.48	24.48	8.44	8.39	11.95	11.94
4-CH ₃	24.43	24.95	8.46	8.53	12.04	12.04
	25.07	—	8.42	8.54	12.00	12.02
3-CH ₃	24.67	24.89	8.41	8.59	12.01	12.04
	24.45	24.88	8.37	8.29	12.04	12.05
3,4-(CH ₃) ₂	25.00	24.85	8.68	8.68	12.20	12.16
	24.99	25.34	8.78	8.79	12.13	12.09
4-Cl	23.85	23.73	8.15	8.16	11.66	11.62
	23.74	24.02	8.03	8.13	11.60	11.60
3-Cl	23.60	23.82	8.02	8.13	11.38	11.37
	23.86	23.63	7.88	7.80	11.37	11.39
3,4-Cl ₂	23.09	22.92	7.84	7.81	11.23	11.16
	23.20	23.33	7.73	7.73	11.13	11.15
4-NO ₂	22.75	22.92	7.58	7.58	11.00	10.93
	22.84	22.97	7.66	7.41	10.97	—
3-NO ₂	23.01	22.80	7.56	7.58	10.97	10.95
	23.08	22.87	7.59	7.61	10.96	10.95
3-OCH ₃	24.33	24.58	8.32	8.29	11.67	11.70
	24.74	24.32	8.24	8.28	11.70	11.74
4-OCH ₃	25.02	25.12	8.61	8.57	12.19	12.13
	24.87	24.80	8.74	8.74	12.21	12.23
4-Br	24.24	24.02	—	—	11.49	11.45
	24.01	23.84	—	—	11.50	—
4-F	24.48	24.26	8.22	8.44	11.73	11.64
	24.16	24.46	8.30	8.41	11.63	—
4-CF ₃	23.22	23.28	7.97	7.97	11.43	11.36
	23.18	23.60	7.97	8.00	11.40	11.32
3-CN	23.25	23.04	7.76	7.65	11.14	11.14
	22.84	23.30	7.59	7.61	11.16	11.15

influence on the dissociation process of the substrate in the given medium. The errors due to the ignorance of the shift of scales in the individual media do not influence this value. From what was given it follows that the pK_{HA} values obtained in various media can be mutually compared from the point of view of the solvent effect on the dissociation process, not from the point of view of the acidity in the individual media.

From the above-mentioned solvent order it follows that with regard to their effect on the dissociation process of sulphonamides the solvents can be divided into three groups: The first group only includes water, which has the lowest pK_{HA} value, thus the substrate is dissociated the most extensively in this solvent. Water stabilizes best the charged particles formed whereby it shifts the equilibrium in favour of formation on these particles. The second group comprises amphiprotic solvents (methanol, ethanol) and dipolar aprotic protophilic solvents (pyridine, dimethyl sulphoxide, dimethylformamide). Amphiprotic alcohols — as compared with water — possess a lower ability to form hydrogen bonds and thereby to stabilize the dissociation products, the electrostatic stabilization being lower, too. The protophilic dipolar

TABLE V

Parameters of the Hammett relation for dissociation of sulphonamides in the individual solvents (for neat solvents arranged according to the magnitude of pK_{HA}^0)

Solvent	pK_{HA}^0	$s_{pK_{HA}^0}$	ρ	s_ρ	r	s	n
water	9.43	0.01	-0.96	0.02	-0.989	0.048	50
pyridine	13.74	0.03	-2.06	0.06	-0.976	0.156	60
methanol	14.39	0.01	-0.52	0.04	-0.903	0.083	51
dimethyl sulphoxide	15.24	0.04	-1.91	0.10	-0.989	0.173	47
ethanol	15.77	0.03	-1.45	0.05	-0.980	0.112	33
dimethylformamide	17.00	0.02	-2.03	0.06	-0.979	0.143	58
acetone	24.51	0.03	-2.22	0.08	-0.966	0.203	59
acetonitrile	24.52	0.02	-2.10	0.04	-0.988	0.113	57
1,2-dichloroethane	25.08	0.02	-1.74	0.06	-0.970	0.148	60
tetramethylene sulphone	31.91	0.02	-2.20	0.06	-0.981	0.149	60
25% methanol	9.64	0.01	-1.11	0.02	-0.994	0.041	55
50% methanol	10.16	0.01	-1.05	0.03	-0.985	0.063	60
75% methanol	10.65	0.01	-1.02	0.03	-0.974	0.080	60
90% methanol	11.28	0.01	-0.83	0.02	-0.975	0.063	60
25% dimethylformamide	10.20	0.01	-1.16	0.02	-0.993	0.049	57
50% dimethylformamide	10.85	0.01	-1.35	0.03	-0.990	0.066	60
75% dimethylformamide	12.01	0.01	-1.66	0.03	-0.991	0.076	60
80% methylcellosolve	11.87	0.01	-1.20	0.03	-0.986	0.062	57
25% acetone	8.40	0.01	-1.09	0.03	-0.974	0.089	56

aprotic solvents show a relatively good ability to split off the proton and thereby to favour the dissociation, but they are worse in stabilizing the conjugated base. The third group of solvents is formed by the protophobic dipolar aprotic solvents (acetone, acetonitrile, 1,2-dichloroethane, tetramethylene sulphone) which do not form hydrogen bonds at all and can stabilize charged particles only by electrostatic action or possibly by weak interactions (polarizability).

It can be expected that sensitivity to substituents in the neat organic solvents investigated will be lower in such cases where the solvent better stabilizes the conjugated base formed and thereby lowers the contribution of substituent to this stabilization. From Table V it follows that a lower sensitivity to substituents is observed in amphiprotic solvents (water, methanol, ethanol). The anomaly encountered with methanol can be due to errors in determination of the pK_{HA} values of the substrates carrying electropositive substituents, these values being found already at the end of the pH^* scale in methanol (the methanol autoprotolysis constant has the value of 16.9, ref.⁷). The sensitivity to substituents observed in dipolar aprotic solvents is similar for protophobic and protophilic solvents. Therefrom it follows that the sensitivity of the dissociation process to substituents is predominantly governed by formation of hydrogen bonds with the conjugated base and is practically unaffected by other types of interactions. The way of solvation of the proton is not decisive.

On going from water to aqueous organic mixtures and neat organic solvents, we can observe a monotonous increase of the pK_{HA}^0 value (except for 25% acetone), hence an addition of an organic solvent worsens the stabilization of the charged particles formed and thereby lowers the dissociation.

The sensitivity to substituents should increase in the direction water \rightarrow organic solvent in accordance with lowered stabilization of the conjugated base. An exception is observed with the water-methanol mixture, where the ρ value decreases with addition of methanol. This fact can be due to a specific solvation of the conjugated base with methanol or to the above-mentioned possible error connected with electro-positive substituents.

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