DETERMINATION OF LIMITING MOLAR CONDUCTIVITIES OF WEAK ORGANIC ACIDS IN AQUEOUS SOLUTIONS

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Received August 3, 1990
Accepted October 19, 1990

Conductance, potentiometric, and spectrophotometric measurements have been made at 25°C of aqueous solutions containing sulfanilic, hippuric, mandelic, and 3,5-dinitrosalicylic acids at different concentrations. Conductance data were analyzed using the methods of Fuoss–Kraus, Kraus–Parker, and Shedlovsky for conductivity of the free ions. Using the calculated limiting conductances, activity coefficients, and degrees of dissociation, the dissociation constants of the weak acids were determined. From plots Λ vs $c^{1/2}$, reliable values for Λ_0 were estimated, using a computer program, and by means of an iterative method the proper value of Λ_0 was determined, independently of that initially introduced. Values of pK were also obtained from potentiometric and spectrophotometric measurements. Evidence for the existence of univalent and divalent ions in aqueous solutions of 3,5-dinitrosalicylic acid was obtained spectrophotometrically, this fact justifying the poorer results provided by conductance measurements.

Limiting conductances of strong electrolytes are important quantities whose magnitudes can be determined by extrapolation to infinite dilution; it is well known that molar conductances are nearly linear in the square root of concentration within the domain of low concentrations, enabling the extrapolation to infinite dilution the determination of $\Lambda_0(\Lambda = \Lambda_0 - \varkappa c^{1/2})$. Same plots for weak electrolytes, however, lead to asymptotic curves at low concentrations that can hardly be extrapolated to infinite dilution to give Λ_0. Limiting conductances for weak electrolytes are usually calculated as the sum of ionic contributions which, in turn, can be calculated from conductance measurements of strong electrolytes by application of Kohlrausch's law of independent ion migration: $\Lambda = \lambda_+^0 + \lambda_-^0$, where λ_i^0, the property of the ion, is the same regardless of what the counterion is.

In this paper, a method for the determination of Λ_0 of weak electrolytes is suggested, consisting of an iterative procedure that takes into account methods of Fuoss–Kraus[1], Kraus–Parker[1], and Shedlovsky[3] as starting point; by introducing an approximated initial value of Λ_0 selected from Λ vs $c^{1/2}$ plot, the final value for Λ_0 is determined independently of that initially introduced. Values for degrees of dissociation, activity coefficients, and distance of closest approach were determined as functions of weak electrolyte concentration.

EXPERIMENTAL

Reactants. The weak acids used were of analytical grade; they were purified by successive crystallizations, with melting points in agreement within ±1°C with literature data. Twice distilled and deionized water was used as solvent with specific conductance under 0·00015 S m^{-1}. Solutions were prepared from stock solutions previously titrated by potentiometry. In order to avoid atmospheric oxidation or photodecomposition[5,6], freshly prepared solutions of sulfanilic acid, isolated from light, were always used over which N_2 gas was bubbled prior to use.

Equipment. Tacussel CD6N conductometer; the Tacussel cell was replatinized and cell constant calculated prior to each set of measurements. A Seta R 100 demineralizer was used for water purification. Potentiometric titrations were carried out with a pHM 62 pH meter (±0·01), ABM 12 autoburette, Rac 61/REA 160 plot recorder, and TTA 60 titration assembly with an Ingold glass electrode. Spectral curves were recorded with a Perkin Elmer 554 UV-vis spectrophotometer with thermostatable cells; the experimental procedure was previously described[13,14]. Experiments were carried out at 25°C with a Selecta Tectron S473 thermostat (±0·01°C). Melting points were determined with a Büchi apparatus (±1°C); this maintains a constant stirring of the bath and permits regulating the rate of increase in temperature.

RESULTS AND DISCUSSION

Figure 1 shows plots Λ vs $c^{1/2}$ for sulfanilic, mandelic, and hippuric acids. Attempts to determine Λ_0 by extrapolation to infinite dilution led to bad results: the lower concentration, the higher the errors in readings, since the solvent contribution to conductance becomes increasingly high at low solute concentrations. For this reason, the lowest concentration utilized was that of conductance about 100 times

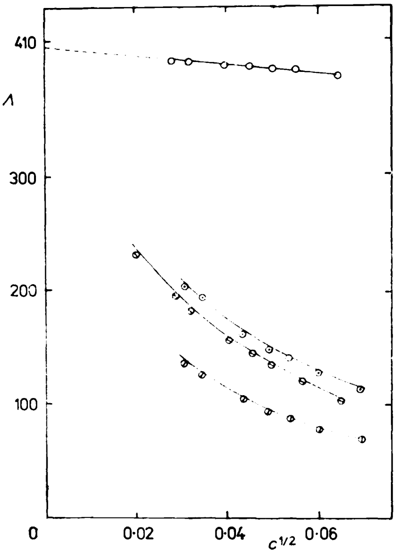

FIG. 1

Variation of molar conductivity with concentration: ○ 3,5-dinitrosalicylic acid, ⊙ sulfanilic acid, ⊗ mandelic acid, and ⊘ hippuric acid higher than the specific solvent conductance, the upper limit of concentration being determined by Debye–Hückel's limiting law.

Accurate determinations of Λ_0 were carried out by choosing some value of Λ within the range whose lower limit was the highest reading, and the upper limit was a reading of Λ arbitrarily chosen, high enough. Using this Λ_0, dissociation degrees and activity coefficients were calculated, enabling the Fuoss–Kraus and Shedlovsky equations be applied:

$$F/\Lambda = 1/\Lambda_0 + c\Lambda f^2/FK\Lambda_0^2 \tag{1}$$

$$1/\Lambda S = 1/\Lambda_0 + cf^2\Lambda S/\Lambda_0^2 K \tag{2}$$

being $F = 1 - Z = 1 - \varkappa(c\Lambda)^{1/2}/\Lambda_0^{3/2}$, K the dissociation constant, and $S^{1/2} = Z/2 + [1 + (Z/2)^2]^{1/2}$; $\varkappa$ denotes the limiting Onsager slope.

From the slope $1/\Lambda_0 K$ and the ordinate $1/\Lambda_0$ of the straight lines (*1*) and (*2*) we can calculate Λ_0 and K. If Λ_0 calculated and that initially introduced are not in good agreement, then, the process is iterated by introducing a second value of Λ_0 from a different subinterval: the initial value of Λ_0 would be the upper or lower limit, depending on whether the second Λ_0 is above or below the first one. The computer program permits testing ranges progressively shorter, until convergence is achieved.

In a similar fashion was used the Kraus–Parker method: an approximate value of Λ_0 is tested and Eq. (*3*) provides an initial value of α; this value is then improved with Eq. (*4*) until convergence is achieved at every concentration.

$$\alpha' = \frac{\Lambda/\Lambda_0}{1 - \varkappa\Lambda_0^{-3/2}(c\Lambda)^{1/2}} \tag{3}$$

$$\alpha'' = \frac{\Lambda/\Lambda_0}{1 - \varkappa\Lambda_0^{-1}(c\alpha')^{1/2}} \tag{4}$$

being

$$X = (1 - \alpha)/\alpha^2 \tag{5}$$

Plots $f(c)^{1/2}$ vs $X^{1/2}$ should lead to straight lines with negligible intercept; however, negative intercepts result if the initial Λ_0 is higher than the proper one. Thus the new interval will range between the initial Λ_0 and one of the ends, the highest in one case, and the lowest in the other. In any event, the slope of the straight line provides $K^{1/2}$.

Based on curves of Fig. 1, the number of iterations to determine Λ_0 and K depends on the magnitude of Λ and on the particular electrolyte; nevertheless, convergence was rapidly achieved in every case. This procedure revealed major usefulness in systems where previous data on ionic conductivities were unavailable and Kohlrausch's law of independent ionic migration became inapplicable; attempts to determine ionic contributions from conductance measurements of strong electrolytes containing the counterion resulted much more cumbersome than direct application of the procedure described. Table I collects results obtained with different methods; the percentage of deviation in conductance progressively decreased with decreasing weak acid concentration, being always lower than 1·5%. As Z is small and F and S are close to unity, the methods of Fuoss–Kraus and Shedlovsky provide results in very good agreement. However, the method of Kraus–Parker was used in this work, since it provides errors lower than 1%. Table II lists results of Λ_0 and pK calculated with different methods, along with statistical parameters of regressions (*1*), (*2*), and (*5*).

TABLE I

Data of concentration c (mol dm^{-3}), conductance L (S), and molar conductivity Λ (S cm^2 . . mol^{-1}) at 25°C. Results of activity coefficients, f, dissociation degrees, α, and molar conductivity, Λ_{cal}, and distance of closest approach, a_0, calculated according to different methods

$c\,.\,10^4$	$L\,.\,10^4$	Λ	Kraus–Parker Method			Fuoss–Kraus and Shedlovsky Methods				a_0, Å
			f	α	Λ_{cal}	$Z\,.\,10^4$	f	α	Λ_{cal}	
Sulfanilic acid										
49·147	5·363	115·77	0·9556	0·3025	116·84	4·651	0·9558	0·2988	114·12	0·506
36·860	4·497	129·38	0·9593	0·3379	130·48	4·269	0·9595	0·3340	127·69	0·496
29·254	3·933	142·52	0·9619	0·3719	143·65	4·002	0·9621	0·3679	140·78	0·486
24·573	3·493	150·60	0·9641	0·3929	151·72	3·795	0·9642	0·3887	148·87	0·478
16·659	3·030	163·21	0·9665	0·4255	164·34	3·412	0·9667	0·4212	161·46	0·469
12·287	2·256	195·30	0·9710	0·5087	196·47	3·010	0·9711	0·5041	193·49	0·465
9·829	1·913	205·54	0·9733	0·5351	206·67	2·693	0·9735	0·5305	203·79	0·459
solvent conductivity = 0·000141 S m^{-1}; cell constant = 0·940 cm^{-1})										
Mandelic acid										
42·751	4·296	105·68	0·9608	0·2694	106·54	4·506	0·9609	0·2687	104·35	0·498
32·060	3·755	123·10	0·9633	0·3136	124·03	4·130	0·9634	0·3130	121·66	0·487
25·652	3·327	136·25	0·9655	0·3470	137·23	3·997	0·9655	0·3465	134·75	0·476
21·375	2·978	146·29	0·9673	0·3724	147·29	3·741	0·9673	0·3720	144·77	0·473
17·100	2·599	159·45	0·9694	0·4057	160·46	3·452	0·9695	0·4054	157·90	0·469
10·687	1·875	183·66	0·9740	0·4669	184·64	2·891	0·9740	0·4670	182·14	0·457
8·552	1·616	197·67	0·9759	0·5023	198·66	2·740	0·9759	0·5026	196·16	0·452
4·275	0·963	234·11	0·9814	0·5942	235·00	2·002	0·9814	0·5922	232·72	0·427
(solvent conductivity = 0·0001572 S m^{-1}; cell constant = 0·947 cm^{-1})										

TABLE I
(*Continued*)

Hippuric acid										
48·798	3·321	71·52	0·9651	0·1857	72·05	4·015	0·9652	0·1855	70·72	0·499
36·599	2·822	80·97	0·9679	0·2103	81·52	3·704	0·9678	0·2100	80·13	0·486
29·279	2·469	88·49	0·9699	0·2300	89·05	3·400	0·9699	0·2295	87·63	0·475
24·399	2·226	96·65	0·9710	0·2507	97·23	3·263	0·9713	0·2506	95·76	0·472
19·519	1·995	107·07	0·9728	0·2779	107·68	3·011	0·9729	0·2777	106·14	0·467
12·199	1·491	127·72	0·9765	0·3315	128·35	2·599	0·9766	0·3312	126·76	0·454
9·758	1·299	138·88	0·9780	0·3604	139·51	1·998	0·9782	0·3601	137·91	0·447
(solvent conductivity = 0·0001629 S m^{-1}; cell constant = 0·947 cm^{-1})										
3,5-Dinitrosalicylic acid										
4·063	1·531	391·18	0·9291	0·960	383·27	7·436	0·9291	0·960	382·26	0·535
3·047	1·131	396·09	0·9379	0·972	389·39	6·480	0·9379	0·972	388·22	0·541
2·438	0·936	398·55	0·9441	0·978	392·57	5·814	0·9441	0·978	391·45	0·542
2·032	0·781	399·34	0·9488	0·980	393·58	5·313	0·9488	0·979	392·84	0·535
1·625	0·627	400·36	0·9540	0·983	394·92	4·758	0·9540	0·982	394·53	0·530
1·016	0·317	402·83	0·9634	0·988	398·36	3·773	0·9634	0·988	398·17	0·518
0·813	0·157	403·91	0·9671	0·991	399·96	3·379	0·9671	0·991	399·73	0·525
(solvent conductivity = 0·0001437 S m^{-1}; cell constant = 0·962 cm^{-1})										

Banks et al.[4] reported values of pK = 3·41 and Λ_0 = 378·77 calculated for mandelic acid from conductance measurements of sodium mandelate and barium mandelate, and Swinehart et al.[5,6] reported values of pK = 3·2281 and 3·7381 calculated for sulfanilic acid from EMF measurements. We also reported values[7] of pK = 3·27 and 3·12, calculated for sulfanilic acid at 25°C by spectrophotometry and potentiometry. On the other hand, values of pK = 3·23, 3·85, and 3·80 (ref.[8]) and 3·12, 3·41, and 3·65 (ref.[9]) have also been reported for sulfanilic, mandelic, and hippuric acids, respectively; according to these values, the results summarized in Table II may be acceptable. Being 349·8 S cm^2 mol^{-1} the limiting conductance of hydrogen ion by itself[10], the following anion contributions are deduced: sulfanilic 37·31, hippuric 36·04, and mandelic 44·29 S cm^2 mol^{-1}, from which the Stokes radii 2·74 Å, 2·55 Å, and 2·08 Å respectively were calculated.

In order to investigate the effect of ionic association, the closest distance between ions a_0 was calculated, based on Bjerrum's theory[10]; these distances were identical (see Table I) irrespective of the methods followed, and are only dependent of the weak acid concentration and the degree of ionic association $(1 - \alpha)$. The small values of a_0 are in agreement with a dissociation process of the type:

$$\underset{I}{\mathrm{AH}\cdots\cdots\mathrm{OH_2}} \rightleftharpoons \underset{II}{\mathrm{A^{-}\,{}^{+}HOH_2}}$$

For weak acids (p$K > 2$), the potential energy curve of the proton exhibits only an asymmetric minimum located at the position of the anion, which confirms that structure *II* does not possess any actual stable existence. Nevertheless, the importance of structure *II* raises as the number of solvent molecules per molecule of weak acid increases, since a polar environment will favour a more polar structure; the opposite will favour structures like *I*. Structure *II* can be detected in moderately strong acids only if concentrations of the free protons and that of structure *I* are similar[12].

TABLE II

Values of Λ_0 (S cm^2 mol^{-1}) and statistical parameters of linear regressions for sulfanilic, mandelic, and hippuric acids according to different methods and techniques

Parameter	Conductometry			Spectrophotometry		Potentiometry
	Fuoss–Kraus	Kraus–Parker	Shedlovsky	Graphic method	$\log I = -n\mathrm{pH} + n\mathrm{p}K$	Graphic method
			Sulfanilic acid			
Λ_0	387·57	386·20	387·57			
pK	3·24 ± 0·01	3·23 ± 0·005	3·24 ± 0·01	3·28 ± 0·01	3·27 ± 0·01	3·25 ± 0·01
r_{xy}	0·9996	0·9998	0·9997		0·9995	
$S(y)$	6·60 10^{-5}	4·24 10^{-4}	4·45 10^{-5}		0·010	
			Mandelic acid			
Λ_0	393·40	395·48	393·39			
pK	3·38 ± 0·04	3·38 ± 0·02	3·38 ± 0·04	3·35 ± 0·01	3·38 ± 0·02	3·40 ± 0·01
r_{xy}	0·9934	0·9972	0·9935		0·9997	
$S(y)$	2·74 10^{-4}	1·40 10^{-4}	3·45 10^{-4}		0·009	
			Hippuric acid			
Λ_0	385·71	386·10	385·71			
pK	3·71 ± 0·02	3·72 ± 0·006	3·71 ± 0·01	—	—	3·67 ± 0·01
r_{xy}	0·9990	0·9996	0·9991			
$S(y)$	1·17 10^{-4}	4·29 10^{-4}	1·01 10^{-4}			

r_{xy} is linear correlation coefficient; $S(y)$ is standard deviations.

To achieve a deeper knowledge of the weak electrolytes investigated, the corresponding dissociation constants were also determined by potentiometry and spectrophotometry. The UV-vis spectral curves of basic and acid forms of hippuric acid showed no noticeable differences; thus this technique was unapplicable for this species. Table II lists the values of equilibrium constants calculated with different methods already put forward[13]: (i) graphic method, according to which pK coincides with the abscissa of the inflexion point of the sigmoid curve absorbance vs pH; (ii) plot $\log I$ (ionization ratio) vs pH, from which the quotient intercept/slope yields pK. By potentiometry, pK are calculated from plots pH vs volume of titrant (NaOH).

3,5-Dinitrosalicylic acid was selected as moderately strong acid to which the conductometric methods described were applied[1–3]. Figure 1 shows plots Λ vs $c^{1/2}$, and Tables I and III collect results of f, α, Λ_0, and pK obtained; Λ_0 calculated by successive iterations and those coming from linear extrapolations Λ vs $c^{1/2}$ are in very good agreement, but results of pK calculated by conductance and spectral measurements did not agree to the required extent. Spectral evidence was obtained of two acid-base equilibria corresponding to ionization of hydroxide (within pH region) and carboxylic (at higher acidities) groups; the first equilibrium was investi-

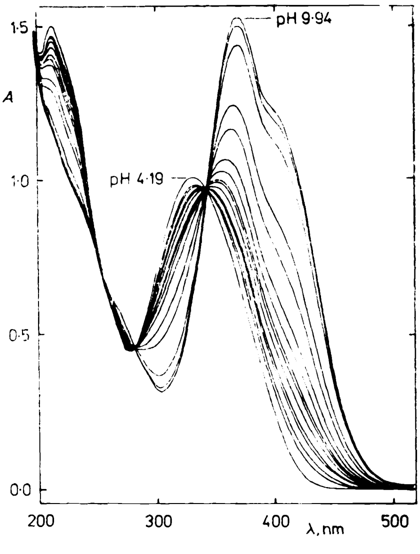

FIG. 2

UV-vis spectral curves corresponding to ionization of 3,5-dinitrosalicylic acid (hydroxide group) within 4·19—9·94 pH

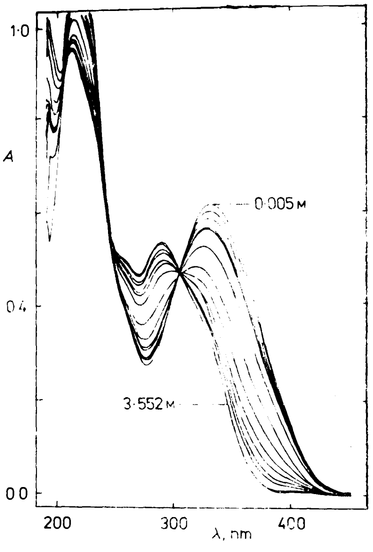

FIG. 3

UV-vis spectral curves corresponding to ionization of 3,5 dinitrosalicylic acid (carboxylic group) within 0·005—3·552M $\mathrm{HClO_4}$

gated using methods already put forward for weak acids[13], whereas the second needed the use of Hammett acidity functions H_0 (refs[14,15]) and excess acidity functions[16–18], according to equations of Hammett, Cox–Yates, and Marziano (see Table III). Thus evidence is shown of the existence of three different ions in aqueous solutions of 3,5-dinitrosalicylic acid,

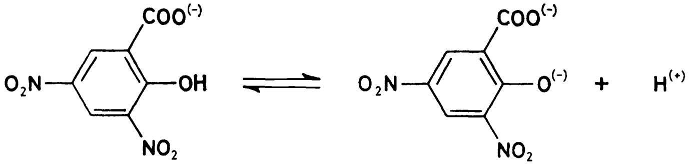

TABLE III

Values of Λ_0 (S cm^2 mol^{-1}) and pK calculated by conductometric and spectrophotometric measurements for 3,5-dinitrosalicylic acid

Conductometry

	Fuoss–Kraus	Kraus–Parker	Shedlovsky
Λ_0	407·72	407·63	407·72
pK	1·7 ± 0·03	1·06 ± 0·05	1·07 ± 0·02
r_{xy}	0·9895	0·9914	0·9892
$S(y)$	4·23 10^{-6}	1·61 10^{-3}	3·15 10^{-6}

Spectrophotometry

Within pH acidity range (hydroxide group)

	graphic method	$\log I = -n\text{pH} + n\text{p}K$
pK	7·60 ± 0·01	7·67 ± 0·35
r_{xy}	—	0·9988
$S(y)$	—	0·0961

High acidity range (carboxylic group)

	H_0 (ref.[14])	H_0 (ref.[15])	X (ref.[16])	X (ref.[17])	M_c (ref.[18])
n	0·899 ± 0·01	0·382 ± 0·01	0·618 ± 0·09	0·661 ± 0·07	0·360 ± 0·03
pK	0·290 ± 0·01	0·304 ± 0·01	0·357 ± 0·09	0·329 ± 0·02	0·345 ± 0·01
r_{xy}	0·9992	0·9991	0·9901	0·9937	0·9831
$S(y)$	0·025	0·032	0·016	0·027	0·025

being this probably the reason for discrepancies between conductance and spectral results. The treatment of conductance data according to Fuoss method was not easily adaptable to solutions containing more than two types of ions, and the treatment for multiple ions was very complex[19]; for our dilute ionic solutions such treatment might result unnecessary, since spectrophotometric techniques permit the calculation of ionization constants of dilute solutions (<0.001 mol l^{-1}) at any acidity level. Finally, it should be pointed out that, due to the lack of references regarding the acid-base behaviour of 3,5-dinitrosalicylic acid, it was firstly treated as univalent electrolyte; nevertheless, further spectral information showed this assumption to be incorrect.

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