234. *The Dissociation Constants of Organic Acids. Part IX. Some Amic Acids.*

By George H. Jeffery and Arthur I. Vogel.

The determination of the primary dissociation constant of a dibasic acid involves a knowledge of the limiting mobility of the HA′ ion. This constant cannot be determined directly from conductivity measurements with the sodium or potassium hydrogen salt, $NaHA \rightleftharpoons HA' + H^{\cdot}$, owing to the secondary ionisation, $HA' \rightleftharpoons A'' + H^{\cdot}$. Chandler (*J. Amer. Chem. Soc.*, 1908, **30**, 694) assumed that the mobility of the acid anion would be the same as that of the most closely related monobasic anion, and compared, *e.g.*, the hydrogen malonate ion, $CO_2H{\cdot}CH_2{\cdot}CO_2'$, with the propionate ion, $CH_3{\cdot}CH_2{\cdot}CO_2'$. In another method, he calculated the mobility from the *empirical* equation $\lambda_{0_{HA'}} = 0{\cdot}6\,\lambda_{0_{A''}}$, where $\lambda_{0_{HA'}}$ and $\lambda_{0_{A''}}$ are the limiting mobilities of the two ions. Vogel (Part I, J., 1929, 1485) assumed $\lambda_{0_{HA'}} = 0{\cdot}5\,\lambda_{0_{A''}}$. Both procedures are clearly only approximate. The development of a new combined solvent and hydrolysis correction for the ionisation of the disodium salts of dibasic acids, $Na_2A \rightleftharpoons 2Na^{\cdot} + A''$ (which will shortly be published), permits of the evaluation of the limiting mobility of the bivalent ion, A'', with some accuracy, and it was therefore clearly desirable to obtain experimental evidence relating this to the limiting mobility of the acid anion. This was achieved by measuring the conductivities of the sodium salts of the corresponding amic acids, $CO_2Na{\cdot}(CR_1R_2)_x{\cdot}CO{\cdot}NH_2$; the ionisation of the secondary hydrogen atom is thus suppressed. Further, consideration of the parachor of the carbamyl and the carboxy-group indicates that the molecular volumes, which will of course affect the mobility, are very approximately equal, and hence a close approximation to the mobility of the acid anion should be obtained. The approximation will be closer the greater the molecular weight of the acid.

Four amic acids ($x = 1$, 2, 3, and 4) were investigated. They were all prepared according to the general scheme :

$$(CH_2)_x{<}\begin{matrix}CO_2Et\\CO_2Et\end{matrix} \longrightarrow (CH_2)_x{<}\begin{matrix}CO_2H\\CO_2Et\end{matrix} \longrightarrow (CH_2)_x{<}\begin{matrix}CO_2NH_4\\CO{\cdot}NH_2\end{matrix} \longrightarrow (CH_2)_x{<}\begin{matrix}CO_2H\\CO{\cdot}NH_2\end{matrix}$$

although, for succinamic and glutaramic acids, another method, involving the use of the anhydrides (see p. 1103), was also employed.

Conductivity measurements of the acid in silica cells and of the sodium salts in Pyrex cells were made over the range 0·0001—0·01*N*. The combined solvent and hydrolysis correction (Part VII, J., 1933, 1637; Part VIII, this vol., p. 166) was applied to the sodium salts, and the true dissociation constants were calculated as previously described (*loc. cit.*). The final results are summarised below.

Acid	Malonamic	Succinamic	Glutaramic	Adipamic
Mobility of anion	35·5	31·5	30·0	28·6
$K_{1\text{therm.}} \times 10^5$.	22·84	2·892	2·510	2·352

The constancy of the dissociation constants above *ca.* 0·001*N* indicates clearly that the dissociation of the carbamyl group, if any, is negligible; the slight variations below this concentration are probably due to the combined influence of the solvent correction and the interaction between the carbonic acid and the amic acid, the effect of which becomes inappreciable at higher concentrations. Where secondary dissociation does occur, as in the normal dibasic acids, the constancy does not appear until about 0·005*N* (unpublished observations).

The relationship between the limiting mobility of the acid anion and of the corresponding bivalent ion will be discussed in a later paper.

Experimental.

Preparation of Materials.—Malonamic acid. Boots's ethyl malonate was converted into ethyl hydrogen malonate, b. p. 145—146°/18 mm., by treatment with potassium hydroxide (Walker, J., 1892, **61**, 711). 21 G. of the acid ester were treated with 35 c.c. of ammonia (*d* 0·88) at 0°, the whole kept in a stoppered bottle in the ice-chest for 48 hours, acidified with ice-cold dilute sulphuric acid, and the liquid extracted several times with diethyl ketone. The extract was dried (sodium sulphate) and the solvent removed under diminished pressure; 9 g. of solid, m. p. 106—110°, remained, which after five recrystallisations from diethyl ketone had m. p. 121° (Found : C, 34·94; H, 4·89. Calc. : C, 34·91; H, 4·85%).

Sodium malonamate was prepared by dissolving a weighed quantity of the acid in absolute ethyl alcohol, and adding, from a carefully calibrated burette, the calculated volume of a standard (approx. *N*/2) solution of sodium ethoxide, prepared by dissolving Kahlbaum's sodium (" pure for analysis ") in absolute alcohol and titrated against standardised hydrochloric acid. The sodium salt gradually separated, and, after filtration, was recrystallised by dissolving it in a *small* quantity of *cold* water and precipitating it by addition of absolute ethyl alcohol (Found : Na, as sulphate, 18·36; N, by distillation with NaOH solution, 11·12. Calc. : Na, 18·41; N, 11·19%).

Succinamic acid. Specimen 1. Succinic acid, A.R., on distillation with pure acetic anhydride yielded the anhydride, b. p. 138—140°/15 mm., m. p. 119° (from chloroform). 20 G. of the anhydride were dissolved in dilute aqueous ammonia, the excess of ammonia expelled by warming on the water-bath, and silver succinamate precipitated by the addition of silver nitrate solution (cf. Hoogewerff and van Dorp, *Rec. trav. chim.*, 1899, **18**, 361). The silver salt was suspended in water and decomposed with hydrogen sulphide, and the solution filtered and evaporated by warming in a vacuum on a water-bath. It is essential to carry out the evaporation under diminished pressure, since at the ordinary pressure the substance is decomposed with the evolution of ammonia. The product (12 g.) was recrystallised from acetone containing a little ether, and melted sharply at 157° (Hoogewerff and van Dorp, *loc. cit.*, give 156—157°).

Specimen 2. 29 G. of methyl hydrogen succinate, m. p. 58°, prepared from succinic anhydride by Bone, Sudborough, and Sprankling's method (J., 1904, **85**, 529), were treated with 42 c.c. of aqueous ammonia (*d* 0·88), and worked up as described for malonamic acid; 15 g. of the acid were isolated, m. p. 157° after two crystallisations.

Sodium succinamate was prepared as described for sodium malonamate (Found : Na, 16·57; N, 10·05. Calc.: Na, 16·56; N, 10·08%).

Glutaramic acid. Specimen 1. Glutaric acid, *ex* nitrile, m. p. 97—98°, was converted into the anhydride, b. p. 160—162°/15 mm., m. p. 57° from chloroform–ether, by distillation with pure acetic anhydride. 10 G. of the anhydride were treated successively with concentrated aqueous ammonia, silver nitrate, and hydrogen sulphide as detailed for succinamic acid, and finally yielded 6 g. of acid, m. p. 93—94°, after recrystallisation from acetone–ether.

Specimen 2. 20 G. of methyl hydrogen glutarate, b. p. 154—156°/14 mm., prepared by refluxing the anhydride with pure dry methyl alcohol, were treated with aqueous ammonia and worked up as usual; 12 g. of glutaramic acid, m. p. 93—94° after recrystallisation, were obtained (Found, for mixture of equal weights of specimens 1 and 2 : C, 45·90; H, 6·84. Calc. for $C_5H_9O_3N$: C, 45·80; H, 6·87%).

Both specimens of the acid, although analytically pure, did not yield constant values for the true dissociation constant, possibly owing to the presence of minute traces of impurities. Each specimen was therefore separately recrystallised three times from ethyl acetate and then employed in the conductivity measurements; m. p. 94°.

Sodium glutaramate was prepared in the usual manner (Found : Na, 15·08; N, 9·23. Calc. for $C_5H_8O_3NNa$: Na, 15·04; N, 9·15%).

Adipamic acid. 20 G. of methyl hydrogen adipate, b. p. 164—166°/18 mm. (Morgan and Walton, J., 1933, 91), were treated with aqueous ammonia as described above, and on acidification a white solid was precipitated which was filtered off, a further quantity being obtained by extraction of the filtrate with diethyl ketone. The yield was 13 g., and the m. p. 161° after recrystallisation from diethyl ketone (Found : C, 49·53; H, 7·61. $C_6H_{11}O_3N$ requires C, 49·67; H, 7·59%). Etaix (*Ann. Chim.*, 1896, **9**, 376) gives m. p. 125—130° for "adipamic acid," which was recrystallised from hot water !

Sodium adipamate was prepared as above (Found : Na, 13·72; N, 8·45. $C_6H_{10}O_3NNa$ requires Na, 13·78; N, 8·38%).

Conductivity Measurements.—The general technique and apparatus were as described in earlier papers of this series. Four cells of the Hartley and Barrett type, two of silica, R ($0·02586_3$) and Q ($0·02674_8$), and two of Pyrex, S ($0·03422_8$) and V ($0·02871_5$), were used; the figures in parentheses are the corresponding cell constants, which were checked at regular intervals by the method described in Part IV (J., 1931, 1719). All the measurements were carried out at 25° ± 0·01°.

Solvent Correction and Calculation of the Dissociation Constants.—No correction was applied to the acid solutions. The combined solvent and hydrolysis correction for the sodium salts was applied as detailed for sodium phenylacetate (this vol., p. 167). The specific conductivity of the water was first subtracted from that observed for the salt, and this gave the following preliminary values :

		Mobility of anion.
Sodium malonamate :	$\Lambda_0^n = \Lambda_c + 481·2\,C^{0·846} = 84·52$..............	34·7
Sodium succinamate :	$\Lambda_0^n = \Lambda_c + 361·4\,C^{0·814} = 80·11$..............	30·3
Sodium glutaramate :	$\Lambda_0^n = \Lambda_c + 177·5\,C^{0·734} = 78·17$..............	28·4
Sodium adipamate :	$\Lambda_0^n = \Lambda_c + 181·1\,C^{0·642} = 76·92$..............	27·1

With the aid of the above mobility figures and one run for each of the acids, the following preliminary classical dissociation constants were computed : malonamic acid, $2·482 \times 10^{-4}$ ($\Lambda_0 = 382·7$); succinamic acid, $3·052 \times 10^{-5}$ ($\Lambda_0 = 378·3$); glutaramic acid, $2·641 \times 10^{-5}$

(Λ_0 = **376·4**); adipamic acid, **2·477** $\times$ 10^{-5} (Λ_0 = **375·1**). The successive stages of the calculations are identical with those previously described (this vol., p. 167).

The final results are tabulated below. For the sodium salts, κ is the specific conductivity of the water used, Λ, norm. is the equivalent conductivity after the application of a normal solvent correction, [H$^{\cdot}$] is the hydrogen-ion concentration computed by means of equation (8) or (10) (J., **1933**, **1639**), Λ, corr. is the conductivity corrected by means of equation (11) (Part VII, J., **1933**, **1639**), C is the concentration in g.-equivs. per litre, Λ_0^n is the value of Λ_0 calculated by means of the " n " formula, the constants of which are given at the head of the table; $\lambda_{0X'}$ is the limiting mobility of the appropriate anion.

For the acids, c'' is the ionic concentration corresponding to the molecular concentration C, calculated as described in Part VI (J., **1932**, **2837**), two approximations being sufficient; Λ_e was obtained from the relationship

$$\Lambda_e CO_2H\cdot(CH_2)_x\cdot CO\cdot NH_2 = \Lambda HCl - \Lambda NaCl + \Lambda CO_2Na\cdot(CH_2)_x\cdot CO\cdot NH_2,$$

the conductivity data for sodium chloride and hydrochloric acid given in Parts IV and V (J., **1931**, **1715**; **1932**, **400**) being employed. $K_{\text{therm.}}$ is the thermodynamic or true dissociation constant, deduced from the equation $\log K_{\text{therm.}} = \log K' - 1{\cdot}010\, c''^{0\cdot5}$, where K' is the dissociation constant computed from the corresponding degree of dissociation $\alpha' = \Lambda_c/\Lambda_e$. The figures in parentheses were not employed in the calculation of the mean.

$C\times10^4$.	Λ, norm.	[H$^{\cdot}$]$\times10^7$.	Λ, corr.	Λ_0^n.	$C\times10^4$.	Λ, norm.	[H$^{\cdot}$]$\times10^7$.	Λ, corr.	Λ_0^n.
				Sodium malonamate (M = 125·04).					
			$\Lambda_0^n = \Lambda_c + 450{\cdot}4C^{0\cdot875}$.	Λ_0^n = 85·31.	$\lambda_{0X'}$ = 35·5.				
	Run 1.	Cell S.	κ = 0·832.			Run 2.	Cell V.	κ = 0·823.	
1·122	84·56	17·13	(85·78)	—	2·498	84·48	15·41	(85·32)	—
5·251	84·10	12·30	84·68	85·29	7·782	83·87	10·01	84·41	85·27
9·930	83·69	8·27	84·18	85·24	15·12	83·29	6·58	83·78	85·31
18·80	82·96	5·93	83·33	85·28	37·61	81·93	3·72	82·01	85·31
29·22	82·35	4·54	82·60	85·33	49·91	81·24	3·15	81·31	(85·67)
43·08	81·71	3·49	81·89	(86·72)	66·12	80·69	2·98	80·72	—
55·39	81·22	3·00	81·29	—	78·06	80·32	2·81	80·31	—
75·51	80·44	2·91	80·46	—	95·42	79·85	2·62	79·85	—
				Sodium succinamate (M = 139·05).					
			$\Lambda_0^n = \Lambda_c + 330{\cdot}0C^{0\cdot843}$.	Λ_0^n = 81·29.	$\lambda_{0X'}$ = 31·5.				
	Run 1.	Cell V.	κ = 0·806.			Run 2.	Cell S.	κ = 0·812.	
1·426	80·23	7·71	(81·72)	—	3·112	80·12	4·16	(81·29)	—
6·829	79·72	3·07	80·44	81·15	5·667	79·80	3·27	80·72	81·32
13·65	79·41	1·98	80·18	81·35	11·23	79·57	2·21	80·19	81·27
28·74	78·66	1·01	78·97	81·34	17·56	79·15	1·56	79·68	81·25
48·89	77·89	0·50	78·01	(81·73)	25·12	78·82	1·13	79·20	81·32
66·43	77·26	0·41	77·32	—	42·24	78·15	0·53	78·27	(81·56)
93·82	76·48	0·30	76·50	—	70·01	77·13	0·39	77·17	—
120·4	75·72	0·11	75·72	—	102·5	76·30	0·22	76·31	—
				Sodium glutaramate (M = 153·07).					
			$\Lambda_0^n = \Lambda_c + 167{\cdot}6C^{0\cdot629}$.	Λ_0^n = 79·83.	$\lambda_{0X'}$ = 30·0.				
	Run 1.	Cell V.	κ = 0·717.			Run 2.	Cell S.	κ = 0·729.	
1·349	76·82	6·33	(79·81)	—	3·112	77·31	5·05	(79·03)	—
6·435	77·40	2·37	78·18	79·83	9·998	77·09	1·87	77·61	79·79
12·36	76·79	1·45	77·22	79·70	17·59	76·43	1·27	76·76	79·86
25·35	75·88	0·80	76·09	79·99	32·51	75·44	0·64	75·64	(80·12)
47·65	74·74	0·46	74·83	(80·63)	45·99	74·77	0·45	74·83	—
66·80	73·94	0·33	74·01	—	57·52	74·28	0·38	74·34	—
86·97	73·42	0·26	73·45	—	73·83	73·75	0·31	73·76	—
105·5	73·10	0·18	73·10	—	96·74	73·25	0·22	73·25	—
				Sodium adipamate (M = 167·09).					
			$\Lambda_0^n = \Lambda_c + 202C^{0\cdot686}$.	Λ_0^n = 78·38.	λ_{0X} = 28·6.				
	Run 1.	Cell V.	κ = 0·724.			Run 2.	Cell S.	κ = 0·716.	
0·975	77·21	7·01	(79·10)	—	3·012	77·01	4·14	(78·01)	—
4·614	76·49	3·56	77·41	78·39	10·05	76·03	2·33	76·41	78·39
8·155	76·28	2·71	76·77	78·31	14·49	75·74	1·81	76·01	78·30
18·56	75·46	1·51	75·67	78·28	29·82	74·58	0·91	74·71	78·46
36·82	74·34	0·68	74·47	(78·81)	43·14	73·86	0·51	73·94	(78·78)
49·33	73·78	0·47	73·87	—	57·52	73·32	0·43	73·39	—
65·12	73·14	0·39	73·19	—	72·25	72·91	0·35	72·92	—
76·90	72·76	0·33	72·76	—	98·14	72·25	0·25	72·25	—

$C \times 10^4$.	Λ_c.	Λ_e.	$c'' \times 10^4$.	$K_{therm.} \times 10^5$.	$C \times 10^4$.	Λ_c.	Λ_e.	$c'' \times 10^4$.	$K_{therm.} \times 10^5$.
Malonamic acid (M = 103·04; Λ_0 = 383·5).									
Run 1.	Cell Q.	κ = 0·671.			Run 2.	Cell R.	κ = 0·692.		
1·466	260·61	383·12	0·9969	(20·71)	2·512	210·23	383·13	1·3782	(20·52)
7·496	156·33	383·03	3·1299	(20·23)	7·306	162·14	383·04	3·0918	(21·74)
12·77	131·12	382·88	4·3721	(22·61)	11·14	138·94	382·94	4·0407	(22·65)
27·38	96·74	382·57	6·9246	22·91	19·08	112·31	382·87	5·5964	22·81
55·05	72·34	382·14	10·3833	22·82	32·57	90·17	382·47	7·6786	22·85
71·84	64·61	381·73	12·1585	22·98	40·04	82·51	382·31	8·6414	22·72
90·21	58·70	381·47	13·8819	22·91	62·99	68·19	381·90	11·2472	22·78
99·44	56·19	381·31	14·6545	22·92	89·12	58·65	381·49	13·7009	22·84
								Mean	22·84
Succinamic acid (M = 117·06; Λ_0 = 379·5).									
Run 1.	Cell R.	κ = 0·768.	Specimen 1.		Run 2.	Cell Q.	κ = 0·784.	Specimen 2.	
2·958	101·20	379·14	0·7897	(2·816)	1·512	137·02	379·15	0·5464	(3·040)
5·619	77·35	379·15	1·1460	(2·866)	3·970	88·01	379·17	0·9215	(2·794)
10·52	58·50	379·16	1·6234	2·882	7·910	65·22	379·16	1·3606	2·881
23·07	40·89	379·14	2·4880	2·899	15·42	49·01	379·15	1·9932	2·894
45·50	30·39	379·05	3·4875	2·911	28·79	36·61	379·10	2·7803	2·889
59·62	26·14	378·98	4·1119	2·906	52·25	27·31	379·01	3·7649	2·881
80·89	22·52	378·90	4·8047	2·886	69·01	24·41	378·96	4·4339	2·914
106·2	19·77	378·83	5·5541	2·888	96·72	20·82	378·85	5·3099	2·870
								Mean	2·892
Glutaramic acid (M = 131·08; Λ_0 = 378·0).									
Run 1.	Cell R.	κ = 0·729.	Specimen 1.		Run 2.	Cell Q.	κ = 0·734.	Specimen 2.	
1·467	132·91	377·35	0·5169	(2·764)	2·457	99·50	377·32	0·6479	(2·278)
7·050	65·38	377·24	1·2218	2·496	7·876	62·21	377·23	1·2989	2·498
12·10	51·19	377·16	1·6423	2·503	19·14	41·42	377·10	2·1018	2·509
25·90	35·93	377·02	2·4685	2·507	29·42	33·85	376·98	2·6417	2·509
46·83	27·15	376·83	3·3735	2·509	37·17	30·31	376·91	2·9891	2·511
65·03	23·20	376·71	4·0041	2·508	55·63	25·01	376·78	3·6926	2·511
87·29	20·17	376·58	4·6751	2·516	75·16	21·68	376·65	4·3262	2·518
101·8	18·75	376·51	5·0667	2·519	91·53	19·72	376·55	4·7394	2·518
								Mean	2·510
Adipamic acid (M = 145·09; Λ_0 = 376·6).									
Run 1.	Cell Q.	κ = 0·603.			Run 2.	Cell R.	κ = 0·618.		
6·046	63·92	376·02	1·0278	(2·056)	1·001	135·75	376·07	0·3613	(2·013)
10·53	50·11	375·99	1·4026	(2·100)	7·317	59·21	376·02	1·1522	(2·100)
20·95	36·90	375·91	2·0557	(2·164)	14·05	44·01	375·96	1·6449	(2·116)
50·32	25·01	375·71	3·3496	2·333	28·87	32·29	375·85	2·4803	2·348
70·02	21·66	375·59	4·0371	2·357	43·09	26·98	375·74	3·0870	2·338
90·55	19·36	375·48	4·6679	2·363	60·76	23·01	375·64	3·7305	2·332
98·46	18·66	375·44	4·9079	2·372	79·12	20·48	375·54	4·3148	2·371
					95·36	18·85	375·47	4·7875	2·365
								Mean	2·352

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