

## The Ionisation Functions of Some Cyanoacetic Acids

By D. J. G. Ives\* and P. G. N. Moseley, The George Senter Laboratory, Birkbeck College, London W.C.1

The thermodynamic functions of ionisation of dimethylcyanoacetic and isopropylcyanoacetic acids from 5 to 45 °C have been determined by an improved conductance method. The data for four cyanoacetic acids are compared in relation to the influence of alkyl substitution and the operation of the compensation law.

THE object of an earlier study<sup>1</sup> was to find how the heat capacity of ionisation ( $\Delta C_p^\circ$ ) of an uncharged acid in water varies with temperature, with the idea that this might show something about the temperature-dependence of the structure of water itself. (Cyanoacetic acid was initially chosen simply because its pK fell within a range favourable to high accuracy of measurement by the conductance method.) The result stimulated this belief, but the accuracy of measurement fell short of that needed for decisive significance. A second attempt,<sup>2</sup> using an alkyl derivative of the first acid (chosen to modify solute hydration), did not support the previous tentative conclusions, indicating that  $\Delta C_p^\circ$  is specifically characteristic of the ionising solute rather than of the solvent. It did, however, draw attention to problems of the hydration of molecules and ions, particularly to the operation of the compensation law.<sup>3</sup> There was, then, need to extend work of this kind to seek definitive answers to the vexed question of the variation of  $\Delta C_p^\circ$  with temperature, and further to study the effects of alkyl substitution on this and other ionisation functions of a parent acid. Two such parent acids have been used: malonic acid (to bring in an anion-acid dissociation) and cyanoacetic acid, with the advantage of comparisons based on their similarity. Results for some malonic acids are in the preceding papers,<sup>4</sup> and comparisons will be made in a later one.<sup>5</sup>

The present work is concerned with the conductimetric evaluation of the ionisation functions of dimethylcyanoacetic ( $\alpha$ -cyano- $\alpha$ -methylpropionic acid) and isopropylcyanoacetic acid ( $\alpha$ -cyano- $\beta$ -methylbutyric acid). These are of additional interest because these substituents have opposite effects on another ionic dissociation equilibrium.<sup>6</sup>

Some new departures were necessary. Improvement in accuracy was sought by use of a new double cell (retaining the four-leads connection system) shown, with its ancillary equipment in Figure 1. It incorporates a mixing chamber to avoid errors due to the Soret effect.<sup>7</sup> Electrodes were lightly platinised but not afterwards sintered. This had the effect of reducing the frequency dependence of apparent resistance to something almost inconsiderable; nevertheless, all measurements were made at two frequencies and extrapolated to infinite frequency.<sup>8</sup> There was a slow temporal drift of cell resistance, negative for potassium chloride solutions,

positive for the acid solutions. Since none of the solutions showed such change when stored in the dispensing flask, and since our procedure had proved adequate to deal with even acute adsorption difficulties,<sup>9</sup> this effect was attributed to leaching of ions from, or ion exchange

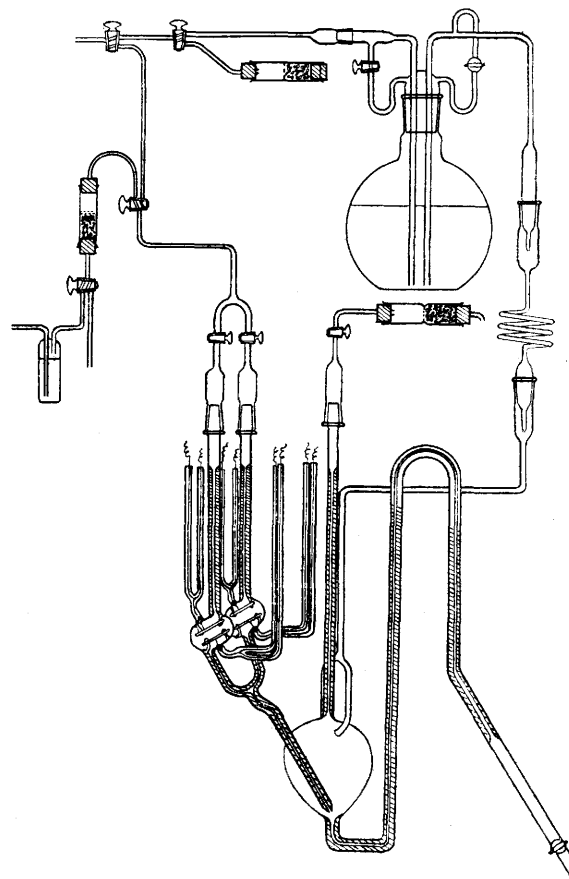


FIGURE 1 New double conductance cell with ancillary equipment

with, the walls of newly-fashioned, unseasoned glass cells of rather large internal area: volume ratio. It was minimised in possible effect by standardisation of sequence and time-scale of operations. Calibration of the cells with a range of potassium chloride solutions<sup>10</sup> and

<sup>1</sup> F. S. Feates and D. J. G. Ives, *J. Chem. Soc.*, 1956, 2798.

<sup>2</sup> D. J. G. Ives and P. D. Marsden, *J. Chem. Soc.*, 1965, 649.

<sup>3</sup> J. E. Leffler, *J. Org. Chem.*, 1955, 20, 1202.

<sup>4</sup> D. J. G. Ives and D. Prasad, preceding paper.

<sup>5</sup> D. J. G. Ives, P. G. N. Moseley, and D. Prasad, in preparation.

<sup>6</sup> D. J. G. Ives, *J. Chem. Soc.*, 1933, 1360.

<sup>7</sup> R. H. Stokes, *J. Phys. Chem.*, 1961, 65, 1277.

<sup>8</sup> F. S. Feates, D. J. G. Ives, and J. H. Pryor, *J. Electrochem. Soc.*, 1956, 103, 580.

<sup>9</sup> D. J. G. Ives and P. G. N. Moseley, *J. Chem. Soc. (B)*, 1966, 757.

<sup>10</sup> J. E. Lind, J. J. Zwolenk, and R. M. Fuoss, *J. Amer. Chem. Soc.*, 1959, 81, 1557.

constant check on resistance ratios were consistent with reliance on 5-figure significance in equivalent conductance.

Availability of computer facilities ('Atlas') allowed methods of treating the data to be reviewed. Equivalent conductances calculated from differences between cell resistances were not systematically greater than those calculated from the separate resistances; this, with the nearly trivial frequency effect, suggested that the double cell technique had lost much of its original purpose. The difference method, designed to eliminate electrode errors, might indeed be disadvantageous if these particular errors had fallen below the level of others of different origin. Other things being equal, data from the cell with the larger cell constant should contain the lesser proportional error, and this at first suggested that nothing would be lost by scrapping the data from the smaller cell. To do this, however, would be to overlook that the latter have some merit of independence of observation—they not only involve a cell with different electrodes, but also the use of a different range of resistances in measurement, and to include them doubles the number of bridge settings contributing to a given result, thereby reducing the effects of random errors of observation. To 'average in' these data by some method giving them appropriate weight would therefore confer statistical benefit. How best to do this was explored by advancing the calculations to the stage of evaluating  $K$  and  $\Lambda_0$  (by the Ives method,<sup>11</sup> which scores over alternatives in that the series of iterations involved are simpler and shorter) for dimethylcyanoacetic acid, to see how the standard errors in these functions might depend on the method of averaging initially used. These errors were found to be (marginally) least when  $K$  and  $\Lambda_0$  were calculated from the arithmetic mean of three values for each solution: those calculated from each cell resistance and from the difference between these resistances.

This apparently odd procedure can be justified by an analysis of errors too long to reproduce. The net result is an average in which the ratio from the larger cell has predominant weight, as considered desirable.

A further new departure was necessary because of Clarke and Glew's critique<sup>12</sup> of the polynomial method of evaluating thermodynamic functions from equilibrium constants. This raises issues of such wider interest as to merit discussion separately elsewhere.

Equivalent conductances are recorded in Tables 1 and 2. The data for the isopropyl acid are restricted because its excessively hygroscopic nature made it unsuitable for complete data processing in relation to the  $\Delta C_p^\circ$  problem. Dissociation constants,  $pK$ , and  $\Lambda_0$  values are in Table 3, the  $\pm$  terms shown being twice the standard error, consistent with the 95% confidence limit.

For the purposes of this paper calculations of the

thermodynamic ionisation functions from the dependence of  $\ln K$  on temperature have again<sup>2</sup> been carried out by the empirical orthogonal polynomial method, within restrictions that err, if at all, on the side of

TABLE 1  
Equivalent conductances of dimethylcyanoacetic acid solutions \*

$10^4 C$ at 25 °C (M)	26.2137	23.3326	19.5277	16.8988	14.8051	12.1362
$T/^\circ\text{C}$						
5	192.21	196.81	203.85	209.19	214.07	220.78
10	210.75	215.97	223.89	229.77	235.30	242.87
15	228.74	234.43	243.25	249.79	255.90	264.36
20	245.93	252.17	261.83	269.10	275.80	285.14
25	262.36	269.16	279.67	287.63	295.02	305.31
30	277.75	285.12	296.56	305.21	313.27	324.45
35	292.21	300.23	312.48	321.88	330.62	342.75
40	305.56	313.97	327.33	337.44	346.82	359.91
45	317.87	326.91	341.07	351.88	361.94	376.02

$10^4 C$ at 25 °C (M)	9.95325	7.34946	6.08877	5.12930	3.85040	2.69855
$T/^\circ\text{C}$						
5	226.75	234.91	239.68	243.14	248.83	254.00
10	249.60	258.85	264.17	268.18	274.57	280.50
15	271.91	282.22	288.28	292.76	299.92	306.65
20	293.60	305.12	311.78	316.83	324.92	332.43
25	314.58	327.33	334.73	340.36	349.37	357.67
30	334.67	348.65	356.87	363.11	373.15	382.32
35	353.91	369.27	378.29	385.20	396.27	406.24
40	372.06	388.83	398.68	406.23	418.42	—
45	389.14	407.23	418.07	426.40	439.72	—

\* It is to be noted that in this and preceding conductance work<sup>1,2</sup> concentrations in  $\text{mol l}^{-1}$  (quoted only at 25 °C) have been used in calculating  $\Lambda$ , ostensibly in  $\text{ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}$ , in disregard of the difference between 1 l and 1000  $\text{cm}^3$ . The maximum error is 0.012 in  $\Lambda$ . The international ohm has also been used, not the absolute ohm. The difference, 0.05% is significant to  $\Lambda_0$ , but not  $K$ .

TABLE 2  
Equivalent conductances of isopropylcyanoacetic acid solutions

$10^4 C$ at 25 °C (M)	19.6972	11.9140	7.15647	5.22761
$T/^\circ\text{C}$				
5	204.22	220.60	234.95	240.97
10	223.96	242.30	258.62	265.58
15	243.13	263.99	282.14	289.91
20	261.55	284.70	304.82	313.57
25	278.42	304.57	326.92	336.81
30	294.93	323.30	348.19	359.05
35	310.72	341.22	368.50	380.74
40	325.19	358.17	388.03	401.37
45	338.48	373.99	406.38	421.09

stringency. If  $\ln K$  is regarded as the determined quantity, the only restriction is that of accepted statistical tests of significance. It is more satisfactory to make an independent assessment (difficult as this may be) of the internal error of the determinations of  $\ln K$ , and to set this beside the statistical tests, either of them to be used appropriately to curb undue optimism. In the present case, we have continued to use  $y$  and  $x$  of the conductance equation (1)<sup>11</sup> as determined quantities, where  $y = \Lambda + aC_i^{\frac{1}{2}}$  and  $x = \Lambda^2 C(10^{-2} AC_i^{\frac{1}{2}})/$

$$y = \Lambda_0 - x/K \quad (1)$$

( $\Lambda_0 - aC_i^{\frac{1}{2}}$ ), with  $C_i$  for ionic concentration,  $a$  and  $\Lambda$

<sup>11</sup> D. J. G. Ives, *J. Chem. Soc.*, 1933, 731.

<sup>12</sup> E. C. W. Clarke and D. N. Glew, *Trans. Faraday Soc.*, 1966, 62, 539.

respectively Onsager limiting slope and Debye-Hückel coefficient. The equation has been solved by the usual iterative procedure (for which a computer programme is available), and  $\Delta y = y_{\text{obs}} - y_{\text{regression}}$  has been examined in relation to  $T$  at constant  $x$  and to  $x$  at constant  $T$ . This has confirmed, as previously, that error in relation to temperature is considerably less than error in relation to concentration. The absence of connection between these two kinds of error leads to the statistical treatment used before,<sup>2</sup> and this has

$t$  is temperature in °C, was fitted to the  $\ln K$  values for dimethylcyanoacetic and isopropylcyanoacetic acids, giving the respective equations (3) and (4),

$$-\ln K = 5.58819 + 5.29338 \times 10^{-2}\xi_1 + 1.71031 \times 10^{-3}\xi_2 - 3.34705 \times 10^{-5}\xi_3 - 9.92220 \times 10^{-6}\xi_4 \quad (3)$$

$$-\ln K = 5.52562 + 6.17425 \times 10^{-2}\xi_1 + 1.17689 \times 10^{-3}\xi_2 \quad (4)$$

higher terms being obviously insignificant.

TABLE 3

Dissociation constants,  $pK$  values, and  $\Lambda_0$  values of dimethylcyanoacetic acid and isopropylcyanoacetic acid in aqueous solution

Temp. °C	Dimethylcyanoacetic			Isopropylcyanoacetic		
	$10^5$ kequiv. $l^{-1}$	$pK$	$\Lambda_0/\text{ohm}^{-1} \text{equiv.}^{-1} \text{cm}^2$	$10^5$ kequiv. $l^{-1}$	$pK$	$\Lambda_0/\text{ohm}^{-1} \text{equiv.}^{-1} \text{cm}^2$
5	454.92 $\pm$ 0.54	2.3420	269.20	501.9	2.299	265.2
10	436.79 $\pm$ 0.52	2.3597	297.93	478.7	2.320	293.3
15	418.22 $\pm$ 0.50	2.3786	326.47	454.2	2.343	321.7
20	398.28 $\pm$ 0.48	2.3998	354.89	431.9	2.365	349.5
25	378.63 $\pm$ 0.46	2.4218	383.02	397.6	2.401	378.3
30	358.25 $\pm$ 0.42	2.4458	410.78	374.3	2.427	405.6
35	338.14 $\pm$ 0.40	2.4709	438.20	353.3	2.452	432.4
40	317.52 $\pm$ 0.38	2.4982	465.19	330.6	2.481	459.0
45	298.29 $\pm$ 0.36	2.5253	491.47	308.3	2.511	485.1
		$\pm 0.0005$	$\pm 0.09$			

been applied to the data for dimethylcyanoacetic acid. The internal variance of  $\ln K$  [variance of  $\ln(K^{-1}/n)$ ] was found to be  $3.92 \times 10^{-7}$ ; the standard

TABLE 4

Standard molar thermodynamic functions for the ionisation of dimethylcyanoacetic acid in aqueous solution

$T/^\circ\text{C}$	5	10	15	20	25
$\Delta G^\circ/\text{cal mol}^{-1}$	2980.7 $\pm 0.6$	3057.3 $\pm 0.4$	3136.7 $\pm 0.3$	3219.0 $\pm 0.3$	3304.2 $\pm 0.4$
$-\Delta H^\circ/\text{cal mol}^{-1}$	1207 $\pm 18$	1360 $\pm 14$	1521 $\pm 10$	1691 $\pm 7$	1870 $\pm 6$
$-T\Delta S^\circ/\text{cal mol}^{-1}$	4188 $\pm 19$	4177 $\pm 14$	4658 $\pm 11$	4910 $\pm 7$	5155 $\pm 6$
$-\Delta S^\circ/\text{cal mol}^{-1}$	15.06 $\pm 0.06$	15.60 $\pm 0.05$	16.16 $\pm 0.04$	16.75 $\pm 0.02$	17.35 $\pm 0.02$
$-\Delta C_p^\circ/\text{cal mol}^{-1}$	29.7 $\pm 1.0$	31.4 $\pm 1.0$	33.1 $\pm 1.0$	34.9 $\pm 1.0$	36.7 $\pm 1.0$
$T/^\circ\text{C}$	30	35	40	45	
$\Delta G^\circ/\text{cal mol}^{-1}$	3392.6 $\pm 0.4$	3484.1 $\pm 0.3$	3578.9 $\pm 0.4$	3677.1 $\pm 0.6$	
$-\Delta H^\circ/\text{cal mol}^{-1}$	2053 $\pm 8$	2256 $\pm 12$	2463 $\pm 18$	2680 $\pm 24$	
$-T\Delta S^\circ/\text{cal mol}^{-1}$	5451 $\pm 8$	5740 $\pm 12$	6042 $\pm 18$	6357 $\pm 25$	
$-\Delta S^\circ/\text{cal mol}^{-1}$	17.98 $\pm 0.02$	18.63 $\pm 0.04$	19.29 $\pm 0.05$	19.98 $\pm 0.07$	
$-\Delta C_p^\circ/\text{cal mol}^{-1}$	38.6 $\pm 1.1$	40.5 $\pm 1.1$	42.4 $\pm 1.2$	44.4 $\pm 1.2$	

error (the square root of this) led to the  $\pm$  terms quoted for  $pK$  in Table 3.

Equation 13 (2),

$$-\ln K = b_0\xi_0 + b_1\xi_1 + \dots + b_6\xi_6 \quad (2)$$

where  $\xi_0 = 1$ ,  $\xi_1 = \phi$ ,  $\xi_2 = \phi^2 - 6.66667$ ,  $\xi_3 = \phi^3 - 11.8000$ ,  $\xi_4 = \phi^4 - 16.4286$ ,  $\xi_5 = \phi^5 - 20.5556$ ,  $\xi_6 = \phi^6 - 24.0909$ , and  $\xi_6 = \phi^6 - 24.0909$ , with  $\phi = (t - 25)/5$ , where

The effects of adding successive polynomial terms were examined as previously.<sup>2</sup> Although the variance ratio (gain from the  $n$ th term/residue from it) remained above unity up to the quintic term, the gain on adding terms higher than the quadratic was less than the internal variance of  $\ln K$ . The  $F$ -test<sup>14</sup> also showed that the inclusion of such terms could not be justified at the 95% significance level.

The thermodynamic ionisation functions calculated on this basis from the first three terms of equation (3), and from equation (4), are in Tables 4 and 5. The

TABLE 5

Standard molar thermodynamic functions for the ionisation of isopropylcyanoacetic acid in aqueous solution

$T/^\circ\text{C}$	5	10	15	20	25
$\Delta G^\circ/\text{cal mol}^{-1}$	2924 $\pm 6$	3006 $\pm 4$	3092 $\pm 4$	3179 $\pm 4$	3269 $\pm 4$
$-\Delta H^\circ/\text{cal mol}^{-1}$	1609 $\pm 224$	1742 $\pm 178$	1882 $\pm 132$	2029 $\pm 90$	2181 $\pm 70$
$-T\Delta S^\circ/\text{cal mol}^{-1}$	4533 $\pm 227$	4749 $\pm 180$	4947 $\pm 134$	5208 $\pm 92$	5451 $\pm 72$
$-\Delta S^\circ/\text{cal mol}^{-1}$	16.3 $\pm 0.8$	16.8 $\pm 0.6$	17.3 $\pm 0.4$	17.8 $\pm 0.3$	18.3 $\pm 0.2$
$-\Delta C_p^\circ/\text{cal mol}^{-1}$	26.1 $\pm 12.2$	27.3 $\pm 12.4$	28.6 $\pm 12.4$	29.9 $\pm 12.5$	31.3 $\pm 12.8$
$T/^\circ\text{C}$	30	35	40	45	
$\Delta G^\circ/\text{cal mol}^{-1}$	3362 $\pm 4$	3457 $\pm 4$	3556 $\pm 5$	3657 $\pm 8$	
$-\Delta H^\circ/\text{cal mol}^{-1}$	2341 $\pm 96$	2508 $\pm 150$	2682 $\pm 218$	2863 $\pm 292$	
$-T\Delta S^\circ/\text{cal mol}^{-1}$	5703 $\pm 98$	5965 $\pm 152$	6237 $\pm 221$	6519 $\pm 296$	
$-\Delta S^\circ/\text{cal mol}^{-1}$	18.8 $\pm 0.3$	19.4 $\pm 0.4$	19.9 $\pm 0.7$	20.5 $\pm 0.9$	
$-\Delta C_p^\circ/\text{cal mol}^{-1}$	32.6 $\pm 13.4$	34.0 $\pm 14.2$	35.5 $\pm 15.0$	36.9 $\pm 16.0$	

<sup>13</sup> J. H. Cadwell, *Computer J.*, 1961, **3**, 266.

<sup>14</sup> D. V. Lindley and J. C. P. Miller, 'Cambridge Elementary Statistical Tables,' Cambridge, 1953, p. 8.

conductance-derived data relate to unimolar standard states; those from e.m.f. measurements in the preceding papers, relate to unimolar standard states.) In relation to  $\Delta C_p^\circ$ , the only worthwhile result is for the dimethyl acid; there is no indication other than a smooth change with rising temperature, albeit in an opposite sense from that previously observed for the di-isopropylcyanoacetic acid.

Further discussion is deferred to a later communication, except for two points. Figure 2 shows plots of  $\Delta H^\circ$

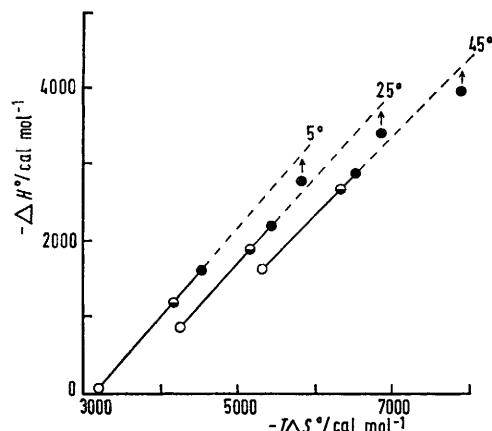


FIGURE 2 Plots of  $\Delta H^\circ$  against  $T\Delta S^\circ$  at three temperatures for the ionisation of cyanoacetic acids in water

against  $T\Delta S^\circ$  for the four cyanoacetic acids for which data are available, at each of the temperatures 5, 25, and 45 °C. The di-isopropyl acid has been disregarded in drawing the lines, making it the somewhat abnormal member of the group. Some justification for this may be found later;<sup>5</sup> as it stands the data for the other three acids are well represented by the linear equations (5).

$$5^\circ: -\Delta H^\circ = 3628 + 1.157T\Delta S^\circ \text{ cal mol}^{-1} \quad (5a)$$

$$25^\circ: -\Delta H^\circ = 3810 + 1.100T\Delta S^\circ \text{ cal mol}^{-1} \quad (5b)$$

$$45^\circ: 3825 + 1.025T\Delta S^\circ \text{ cal mol}^{-1} \quad (5c)$$

At all three temperatures  $\Delta H^\circ$  for di-isopropylcyanoacetic acid is less negative than required by these expressions by a constant amount:  $370 \pm 13 \text{ cal mol}^{-1}$ .

It is clear that marked compensation accompanies alkyl substitution; that is to say, the effects on  $\Delta H^\circ$  and  $T\Delta S^\circ$  are quite large, but mutually compensating, leaving little effect on  $\Delta G^\circ$ . Perfect compensation would, of course, require the coefficient of  $T\Delta S^\circ$  in equations (5) to be unity. This condition is approached as temperature rises and  $\Delta S^\circ$  becomes more negative.

There can be no doubt that the large, negative  $\Delta S^\circ$  for the ionisation of an uncharged acid in water is mainly due to hydrational effects. Following a previous argument,<sup>2</sup> we assign  $\Delta S^h$  to these effects, together with analogous contributions,  $\Delta H^h$  and  $\Delta G^h$ , to the

other thermodynamic functions of ionisation. But, on the assumption that all hydrational systems remain in equilibrium with one and the same bulk solvent,  $\Delta G^h$  is always zero. Hence the non-zero terms  $\Delta H^h$  and  $T\Delta S^h$  must always be equal; there is always perfect compensation in what has been called 'the associated solvent reaction.' It is inferred that the alkyl substitution of cyanoacetic acid exerts its effects on ionisation behaviour largely modifying hydration, and that with increasing temperature these ionisation equilibria pass increasingly under 'solvent control.' This is consistent with an earlier discussion in a wider context.<sup>2</sup>

The second point concerns the temperature coefficient of the Walden product  $[1/(\eta_0\lambda_0)] \cdot \partial\eta_0\lambda_0/\partial T$  for the cyanoacetate ions, excluding the isopropylcyanoacetate ion because of inadequate accuracy. The values (average for the range 5–45 °C) are compared with entropies of ionisation at 25 °C in Table 6.

TABLE 6

	$\frac{10^4}{\eta_0\lambda_0} \cdot \frac{\partial\eta_0\lambda_0}{\partial T}$	$\Delta S^\circ/\text{cal K}^{-1}$
Cyanoacetate	−5.9	−14.3
Dimethylcyanoacetate	+5.8	−17.4
Di-isopropylcyanoacetate	+18.9	−23.1

It can hardly be doubted that there is a connection between these figures which support our thesis that alkyl substitution has a far more fundamental and subtle effect on hydration than has hitherto been supposed. This argument is developed later.<sup>5</sup>

#### EXPERIMENTAL

Apparatus and measurement procedure, except for modifications previously described, were the same as in recent work.<sup>2,9</sup>

Dimethylcyanoacetic acid was prepared by the usual condensation method<sup>15</sup> and purified *via* potassium or barium salt, with regeneration of the acid by means of Amberlite IR-120(H). The aqueous solution of the acid was vacuum-evaporated, with aid of added ethanol, and the dry product sublimed in a high vacuum. The pure acid is hygroscopic; it was handled in a dry-box and weighed in closed capsules. Its density (for buoyancy corrections) is  $1.130 \text{ g ml}^{-1}$ ; m.p. (determined in vacuum apparatus at  $0.1^\circ \text{ min}^{-1}$  heating rate)  $56.4\text{--}56.8^\circ$  (lit.,<sup>9</sup>  $56\text{--}57^\circ$ ) [Found: equiv. (by glass electrode differential titration with carbonate-free NaOH), 113.10. Calc. for  $\text{C}_5\text{H}_7\text{NO}_2$ : equiv., 113.12].

Isopropylcyanoacetic acid was prepared and purified similarly. It is intensely hygroscopic and low-melting, but was obtained in well-crystalline form by molecular distillation, m.p.  $33.8^\circ$  [Found: equiv. (by titration as above), 127.20. Calc. for  $\text{C}_6\text{H}_9\text{NO}_2$ : equiv., 127.15].

We thank the University of Khartoum for a Senior Scholarship (to P. G. N. M.).

[0266 Received, February 16th, 1970]

<sup>15</sup> J. Hessler, *J. Amer. Chem. Soc.*, 1913, **35**, 990.