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THE THERMODYNAMICS OF IONIZATION OF SOME FATTY ACIDS IN FORMAMIDE

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ABSTRACT

The ionization constants of some fatty acids, such as propionic, n-butyric, n-valeric, n-hexoic, iso-butyric, iso-valeric and iso-hexoic, have been determined in formamide over the temperature range 5–45 °C. The thermodynamic quantities associated with the ionization processes of these acids have been evaluated. These quantities are discussed in relation to the structure of the acid and the orientation of solvent molecules by the ions.

INTRODUCTION

In a previous communication[1], we reported the effect of substituents on the strength of acetic acid in formamide from the ionization constants of acetic acid and of chloro- and phenyl- substituted acetic acids in this solvent. This work has now been extended to obtain a reliable assessment of the thermodynamics of ionization of acids of acetic acid series, such as propionic, n-butyric, n-valeric, n-hexoic, iso-butyric, iso-valeric and iso-hexoic acids in this solvent. The method involves measurement of the e.m.f. of cells of type,

$$\text{Ag–AgCl} \mid \text{KCl}(m_3), \text{KA}(m_2), \text{HA}(m_1), \text{QH}_2\text{–Q} \mid \text{Pt} \qquad \text{(A)}$$

where HA stands for the fatty acids, and KA for their potassium salts.

EXPERIMENTAL

Propionic (B.D.H., L.R.), n-butyric, n-valeric, n-hexoic, iso-butyric, iso-valeric and iso-hexoic acids (C.P) were purified by distillation[2]. The purity of these acids was checked by titrations against standard alkali. Potassium salts of these acids were prepared by the method described earlier[3]. Methods of purification of formamide (Reidel, pure) and potassium chloride (B.D.H, AnalaR) have been described in previous communications[3,4]. The potassium salts were kept in a vacuum desiccator over calcium chloride until required.

The detailed description of the apparatus, preparation of the electrodes, design of the cells, preparation of the cell solutions, and e.m.f. measurements have been discussed in earlier work[5]. The reproducibility of the results was of the order of 0.2 mV.

RESULTS AND DISCUSSION

As usual[3,5], values of pK_a were obtained from the e.m.f. of cell (A) by extrapolation of pK_a' to zero ionic strength, μ where $\mu = m_2 + m_3$. The pK'_a is then defined by[3,5]

$$pK_a' = [E - E^\circ(\text{Ag-AgCl}) + E^\circ(\text{QH}_2\text{-Q})]\,F/2.303\,RT + \log(m_1 m_3/m_2) \qquad (1)$$

where E is the observed e.m.f., E°'s are the standard e.m.f.'s, which are known[6] over the temperature range under investigation, and m_1, m_2, and m_3 are the molalities of acid, potassium salt and potassium chloride, respectively.

The pK_a values of these fatty acids at different temperatures in formamide are presented in Table I along with their accuracies. For completeness, data for acetic acid[7] in formamide are also included. It is observed that an increase in temperature has the general effect of lowering the pK_a values of these acids. However, irregularities are noticed at higher temperatures[1,6-11] for which there is no ready explanation. These might be due to structural changes occurring in the hydrogen bonded solvent with the change of temperature. A comparison of the present data with the corresponding values in water[2,12] shows that the pK_a values are higher in formamide than water. This is consistent with the behaviour of other weak acids studied in solvents of this class[1,3,5-11].

The thermodynamic functions for dissociation of the monocarboxylic aliphatic

TABLE I

VALUES FOR pK_a OF FATTY ACIDS IN FORMAMIDE AT DIFFERENT TEMPERATURES

	Temperature (°C)								
Acid	5	10	15	20	25	30	35	40	45
Acetic	7.23	7.13	6.58	6.92	6.96	6.84	6.79	6.71	6.73
Propionic	7.56 ± 0.02	7.41 ± 0.03	7.36 ± 0.03	7.21 ± 0.03	7.26 ± 0.03	7.20 ± 0.02	7.22 ± 0.03	7.16 ± 0.03	7.13 ± 0.03
Butyric	7.45 ± 0.03	7.46 ± 0.02	7.51 ± 0.03	7.36 ± 0.03	7.34 ± 0.02	7.29 ± 0.02	7.26 ± 0.02	7.13 ± 0.04	7.14 ± 0.02
Valeric	7.92 ± 0.03	7.58 ± 0.04	7.75 ± 0.05	7.79 ± 0.05	7.78 ± 0.03	7.67 ± 0.02	7.63 ± 0.04	7.48 ± 0.03	7.61 ± 0.04
Hexoic	7.53 ± 0.04	7.45 ± 0.04	7.39 ± 0.05	7.31 ± 0.06	7.23 ± 0.07	7.17 ± 0.06	7.15 ± 0.02	7.11 ± 0.01	7.08 ± 0.01
iso-Butyric	7.66 ± 0.01	7.63 ± 0.02	7.65 ± 0.04	7.56 ± 0.02	7.47 ± 0.02	7.33 ± 0.01	7.26 ± 0.01	7.30 ± 0.01	7.32 ± 0.01
iso-Valeric	7.70 ± 0.007	7.60 ± 0.02	7.69 ± 0.02	7.62 ± 0.02	7.53 ± 0.008	7.49 ± 0.003	7.47 ± 0.02	7.38 ± 0.02	7.42 ± 0.02
iso-Hexoic	7.11 ± 0.08	7.29 ± 0.02	7.19 ± 0.02	7.20 ± 0.02	7.16 ± 0.003	6.98 ± 0.01	7.00 ± 0.004	6.89 ± 0.006	6.79 ± 0.006

acids in aqueous solutions have been reported[2]. No work appears to have been carried out in formamide medium. However, the pK_a value (7.02) of propionic acid[13] has only been determined in this solvent at 25 °C. The agreement with our value (7.26) is, however, rather less satisfactory. There seems no obvious explanation of this discrepancy. Such differences exist even in very accurate determinations of equilibrium constants by different, or the same, physical methods, examples are plentiful in the literature[1-14]. Since it is found from Table 1 that the pK_a values obtained in the present study agreed within 0.05 to 0.13 units at different temperatures, it seems fairly certain that the present set of data on the pK_a values appears to be more reliable.

It is of interest to examine the relative strength of fatty acids in formamide medium and to compare it with that in water. Considering the pK_a values for these fatty acids at 25 °C, their strengths appear in the order: valeric $>$ iso-valeric $>$ iso-butyric $>$ butyric $>$ propionic $>$ hexoic $>$ iso-hexoic $>$ acetic, in formamide; and propionic $>$ hexoic $>$ iso-butyric $>$ iso-hexoic $>$ valeric $>$ butyric $>$ iso-valeric $>$ acetic, in water.

It is interesting to note a similar behaviour of acetic acid in this series in both formamide and water media. Further, it is observed that the pK_a values in formamide increase as the chain length increases, hexoic acid being an exception. Such a trend is also observed in water, excepting propionic acid, for the n-acid series. It seems, therefore, that hexoic and proponic acids are anomalous in this series but the sequence propionic $>$ hexoic appears more promising in both media.

Table 2 gives the thermodynamic functions of these acids in formamide at 25 °C, together with the corresponding values in water for the sake of comparison. Assuming the heat of ionization to be constant over the entire temperature range, the ΔH° values for the ionization of these acids have been evaluated from the slopes of the plots of pK_a versus $1/T$. The standard free energy change, ΔG° for the ionization process of the acids is obtained from the relation

$$\Delta G^\circ = 2.303\ RT\,\mathrm{p}K_a$$

TABLE 2

THERMODYNAMIC QUANTITIES FOR MONOCARBOXYLIC ALIPHATIC ACIDS IN (*a*) FORMAMIDE AND (*b*) WATER AT 25 °C

Acid	ΔG° (J mole^{-1})		ΔH° (J mole^{-1})		ΔS° (J deg^{-1} mole^{-1})	
	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)
Acetic	397,10	271,45	200.50	− 439	−65.97	− 92.5
Propionic	414,22	278,25	157,89	− 962	−86.02	− 96.5
Butyric	418,78	275,04	156.90	−2996	−87.58	−102.3
Valeric	443,89	276,38	158,30	−3012	−95.84	−102.8
Hexoic	412,50	277,21	195,45	−2925	−72.84	−102.8
iso-Butyric	426,20	276,73	190,33	−3343	−79.15	−104.0
iso-Valeric	429,62	272,85	132,38	−5100	−99.75	−108.6
iso-Hexoic	408,51	276,56	170,87	−2996	−79.75	−102.8

and the standard entropy change, ΔS° is evaluated from the relation

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T.$$

From Table 2, it is evident that the increase in standard free energy of ionization from water to formamide is due to an increase in the electrostatic free energies of the ions in formamide in comparison with that in water. It is seen that the change in free energy varies with the chain length in the n-acids, reaching a maximum value at valeric acid, and pointing to the fact that valeric acid is more solvated than the other n-acids in formamide. The change in entropy of ionization also varies with the chain length in the n-acids and reaches a minimum value at valeric acid.

The values of ΔS° in both formamide and water are expected to be negative, but in formamide they appear to be less negative. The reason for this might be that the degree of re-orientation and partial immobilization of the formamide molecules by anions is not greater in formamide than in water. Further, the negative values of ΔS° for valeric and iso-valeric acids in formamide as compared with the other acids in the series, might indicate that the stabilization of the solvent structure causes an increased order in the proximity of molecules of the ionized form of valeric and iso-valeric acids only. The contrary variation of ΔH° in formamide and water indicates that the ionization reaction is significantly altered when the aqueous medium is replaced by formamide.

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