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Heats of Dissolution of *n*-Fatty Acids in Ethanol

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The heats of dissolution (ΔH_d) of B polymorph of 1-tetradecanoic acid (C14), 1-pentadecanoic acid (C15), 1-hexadecanoic acid (C16), 1-heptadecanoic acid (C17) and 1-octadecanoic acid (C18) were measured at 310.15 K in ethanol using a calorimetric technique. In ethanol, no concentration dependence of ΔH_d was found within the concentration range of at least 1×10^{-3}—2×10^{-2} mol dm^{-3}. At a concentration of 1×10^{-2} mol dm^{-3}, the values of ΔH_d were 60.6, 66.0, 69.4, 75.6 and 79.1 kJ mol^{-1} for C14, C15, C16, C17 and C18, respectively. ΔH_d increased linearly by increasing the number of carbon atoms (*n*) in the fatty acid (FA), so that the (CH_2)-increment was obtained as 4.40 ± 0.10 kJ mol^{-1}.

ΔH_d was compared with the heats of fusion (ΔH_f). ΔH_d was higher than ΔH_f, and the difference between ΔH_d and ΔH_f for odd-numbered FA was larger than that for even-numbered FA. This is related to the phenomena that the plots of ΔH_f *vs.* *n* indicate a zig-zag pattern and those of ΔH_d *vs.* *n* indicate a single line pattern.

Keywords dissolution heat; fatty acid; B polymorph; ethanol; calorimetric technique; fusion heat; molar heat capacity; odd-even effect; melting temperature; transition temperature

The linear alkanoic acids constitute a homologous series which is of considerable importance for industry, biology and pharmaceutics. The physicochemical properties of alkanoic acids have been studied with regard to the triple-point temperatures (T_{tp}),[1] which are nearly equal to the melting points (mp), the molar heat capacities (C_p)[1,2] and the heats of fusion (ΔH_f).[1-3] In living matter both even- and odd-numbered alkanoic acids occur up to hexanoic. Furthermore, alkanoic acids have been found to occur in three main polymorphic modifications, A, B and C. In none of them do the chains rotate in contrast to the α-forms of 1-alkanols: they differ in the angle of the chains with respect to the plane of the carboxyl groups, A = chains vertical; B = chains tilted at 74°40′; C = chains tilted at 59°12′.[4] The latter two are easily crystallized. In addition, the transition temperatures of alkanoic acids have been reported.[1,5]

Regarding the heats of dissolution (ΔH_d), ΔH_d of octadecanoic acid in decane, cyclohexane, methanol and butanone,[6] hexadecanoic acid in benzene,[4] hexanoic, octanoic, decanoic, dodecanoic and tetradecanoic acids in benzene,[7] hexanoic and octanoic acids in pure water,[8] butanoic and hexanoic acids in octane[9] and octanoic acid in octane, benzene, carbontetrachloride and chloroform[10] have been measured. In addition, it has been reported[4,6] that ΔH_d for B polymorph is larger than that for C polymorph.

In contrast to the relatively numerous studies for even-numbered alkanoic acids, only a few studies on ΔH_d for odd-numbered alkanoic acids have been reported; namely, ΔH_d of pentanoic acid in pure water,[8] pentanoic and heptanoic acids in octane[9] and heptanoic and nonanoic acids in octane, benzene, carbontetrachloride and chloroform.[10] However, these studies were carried out only for the liquid state of alkanoic acids. Systematic measurements of ΔH_d for the solid states of continuous odd-even alkanoic acids have not yet been published.

The plots of T_{tp} and ΔH_f against the numbers of carbon atom (*n*) in alkanoic acids indicate zig-zag patterns which indicate an upward convex at even-numbered positions as can be seen in Fig. 1(b), while the plots of C_p *vs.* *n* indicate a single line pattern as can be seen in Fig. 1(c). Therefore, it is very interesting to see which pattern will emerge for the plots of ΔH_d *vs.* *n*.

On the other hand, it has recently been reported that fatty acids (FA) form crystalline complexes with thiamine disulfide (TDS) or nicotinamide (NA) whose molar ratios are 6 : 1 and 1 : 1, respectively.[11] In addition, it is suggested from studies on the release of TDS from FA–TDS complexes that the binding force between FA and TDS is not so strong[12] and that FA–TDS complexes have a property of inclusion compound.[12b] However, further details have not yet been obtained. We are now measuring the ΔH_d of FA–TDS complexes and FA–NA complexes. For the purpose of estimating the binding forces between FA and (TDS or NA), it is essentially necessary to know the ΔH_d of FA. For the measurements of ΔH_d, it is necessary to choose a proper solvent in which FA, TDS and NA are easily dissolved. Furthermore, solvents in which FA exist only as monomeric species are good for accurate analysis of the binding forces between FA complexes and for accurate analysis of the so called "odd-even effect": for example, alkanoic acids in octane, benzene, carbontetrachloride and chloroform exist as equilibrium mixtures of monomer and dimer molecules, and the relationships between ΔH_d of heptanoic, octanoic and nonanoic acids in those solvents and *n* indicate irregular patterns because of the difference in the ratio of monomer and dimer in each solvent.[10]

From these points of view, ΔH_d of 1-tetradecanoic acid (C14), 1-pentadecanoic acid (C15), 1-hexadecanoic acid (C16), 1-heptadecanoic acid (C17) and 1-octadecanoic acid (C18) in ethanol were measured, and the odd-even effect in ΔH_d was compared with that of ΔH_f and C_p.

Experimental

Materials C14, C16 and C18 purchased from P-L Biochemicals, Inc. and C15 and C17 purchased from Sigma Chemicals Co., Ltd. were of guaranteed reagent grade, and these FA were purified by slow crystallization in benzene at room temperatures as described by Beckmann *et al.*[6a] to obtain pure B-form polymorph. Purities of FA were examined by gas chromatography, and every FA had a purity better than 99.8%. The polymorphic modification was checked by obtaining the powder X-ray diffraction patterns as described by Beckmann *et al.*[6a] The patterns showed no amount of the undesired polymorph. Absolute ethanol of the purest grade was obtained from Wako Pure Chemical Industries, Ltd. and was boiled with calcium hydroxide and distilled twice with metal natrium. For each calorimetric measurement, freshly distilled ethanol was used.

Conditioning of Samples FA were filled into small glass ampoules (2 ml capacity), then the ampoules were sealed at their necks by the use of a small gas flame. For C14 and C15 which have a relatively low mp, the ampoule bodies were chilled by cold paper during the sealing procedure to avoid possible changes in their crystalline forms, because there is a report[4)] that B-form is transformed into C-form by cooling the melt. The sealed ampoules were kept in a calorimeter maintained at 310.15 K until the thermal equilibrium was established, whereby 310.15 K was a temperature lower than both the mp and the transition temperatures[1,5)] of FA. For C14 and C15 kept in the sealed ampoules at 310.15 K for 24 h, no transformations were found by measuring the powder X-ray diffraction patterns.

Measurement of ΔH_d The apparatus for the measurement of ΔH_d consists of a twin differential conduction-type microcalorimeter (model TIC-22 of Tokyo Riko Co., Ltd.) and a recorder (model CU-228 of Tokyo Riko Co., Ltd.). About 0.2 g of FA sealed into glass ampoules were immersed into 100 ml of ethanol (final concentration is approximately 1×10^{-2} mol dm^{-3}). As a blank test, a glass ampoule without FA was used. For C18, ΔH_d was measured at various concentrations. All measurements were carried out at 310.15 K. At this temperature, sufficient quantities of C18 dissolve in ethanol, so that a good signal-to-noise ratio is obtained. The ethanol solvent in the cell was stirred (360 rpm) for 18 h in a calorimeter at 310.15 K in order to establish thermal equilibrium. After thermal equilibrium had been established, each glass ampoule was broken open, and the heat absorbed was estimated from the temperature decrease due to the dissolution of FA in ethanol, by the use of a thermomodule. FA dissolve quickly, the measured heat absorption being always virtually finished in less than 2 min. For the measurements of ΔH_d, the sensitivities of the calorimeter were 1 and 5 mV full-scale ranges. The heat absorbed from the actual runs were in the order of 10 J, so that good reproducibilities could be expected. The reproducibility was estimated by measuring ΔH_d for each FA at a constant concentration at least five times. The uncertainty was given by twice the standard deviation of the mean of five experiments.

Accuracy and precision of the calorimeter system was confirmed by measuring ΔH_d of potassium chloride in water at 298.15 K. The observed value agreed well with the value (17.35 kJ mol^{-1})[13)] with an error of about −0.5%.

Results

Effect of Concentration on ΔH_d ΔH_d of C18 was examined as to whether the concentration dependence would be found. For the purpose of examination, the final solution concentration of C18 was 1×10^{-3}, 5×10^{-3}, 1×10^{-2} and 2×10^{-2} mol dm^{-3}. C18 dissolves endothermally in ethanol. This, of course, is attributed to the breaking down of the crystal structure in the course of the dissolution process. The values of ΔH_d of C18 at four concentrations were shown in Table I. For ethanol as a solvent, ΔH_d was nearly constant within this concentration range as can be seen in Table I. This is a similar phenomenon to that observed by Beckmann *et al.*[6a)] in which the concentration dependence of ΔH_d of C18 is negligible in methanol. However, the experimental errors were larger for the runs with lower concentrations.

C18 forms cyclic dimers in the solid state.[14)] The dimers completely dissociate to the monomers in methanol or ethanol, so that no concentration dependence is found. This corresponds to the fact[15)] that no aggregation occurs in methanol and ethanol.

Table I. Heats of Dissolution, ΔH_d, of C18 in Ethanol at 310.15 K with Varying Final Concentrations

C (mol dm^{-3})	ΔH_d (kJ mol^{-1})
1×10^{-3}	78.3 ± 1.8
5×10^{-3}	78.8 ± 0.6
1×10^{-2}	79.1 ± 0.2
2×10^{-2}	79.0 ± 0.2

On the other hand, a decrease of ΔH_d with an increasing concentration can be seen for the dissolution of C18 in decane[6a)] and benzene.[7)] These are considered to be due to the fact that many monomeric species exist at lower concentrations and that dimeric species increase with increasing concentrations.

The acid molecules are paired not only in the crystalline state[14)] but also in the liquid state.[16)] The process of dissolution is, therefore, represented schematically as follows:

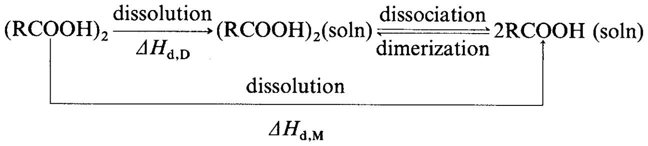

Chart 1

where $(RCOOH)_2$ and RCOOH are dimer and monomer, respectively, and subscripts D and M refer to the monomeric and dimeric acid forms, respectively. Lai and Kertes[10)] measured the standard enthalpies of a solution of heptanoic, octanoic and nonanoic acids for both the monomeric and the dimeric forms, and it has been made clear that the enthalpies of dimerization are exothermic (ΔH negative). Therefore, the positive value of ΔH_d for dissolution with a partial dissociation is smaller than that for dissolution with a complete dissociation, as is recognized from Chart 1.

The values of ΔH_d for B polymorph of C18 at a concentration of 2×10^{-2} mol dm^{-3} and 30.8°C were obtained as 70.6 kJ mol^{-1} in decane and 81.3 kJ mol^{-1} in methanol,[6a)] indicating that the value in methanol is larger because of the establishment of complete dissociation.

Values of ΔH_d of C14, C15, C16, C17 and C18 As described in the previous section, it has been found that the dependence of ΔH_d with concentration is negligible. Therefore, ΔH_d of C14, C15, C16 and C17 at a concentration of 1×10^{-2} mol dm^{-3} in ethanol were determined, and the results were summarized in Table II. Regarding the values of ΔH_d for B polymorph of FA, a value of 81.3 kJ mol^{-1} was obtained for C18 in methanol at 30.8°C.[6a)] The values of ΔH_d for C16 in benzene at a concentration of 3×10^{-2} mol dm^{-3} and 25°C were reported as 66.5 kJ mol^{-1}[4)] and 61.9 kJ mol^{-1}.[7)] In addition, ΔH_d for C14 in benzene at a concentration of 3×10^{-2} mol dm^{-3} and 25°C was obtained[7)] as approximately 53 kJ mol^{-1}. ΔH_d in benzene depends on the concentration of FA: FA exist as monomeric species at low solute concentrations, but FA tend to associate at concentrations above about 1×10^{-2} mol dm^{-3}.[7)] In ethanol, the larger value of ΔH_d is expected

Table II. Heats of Dissolution, ΔH_d, of C14, C15, C16, C17 and C18 in Ethanol at 310.15 K

FA	ΔH_d (kJ mol^{-1})
C14	60.6 ± 0.3
C15	66.0 ± 0.3
C16	69.4 ± 0.4
C17	75.6 ± 0.6
C18	79.1 ± 0.2

Final concentration is 1×10^{-2} mol dm^{-3}.

for the dissolution of FA because of a complete dissociation. Therefore, the obtained larger values of ΔH_d for FA in ethanol than the values[4,7] in benzene are reasonable. Furthermore, it has been reported[8] that the temperature dependence on the value of ΔH_d is small within a narrow temperature range. It is, therefore, considered that our value of 79.1 kJ mol^{-1} for C18 in ethanol at 310.15 K is reasonable with respect to the value[6a] of 81.3 kJ mol^{-1} for C18 in methanol at 303.95 K taking into account the difference in the polarity of the solvents, ethanol and methanol.

Discussion

Effect of Alkyl Chain Length of FA on ΔH_d Dissolution is the phenomenon that a uniform liquid phase is formed when a solid is mixed in a liquid. ΔH_d is the difference in the thermal quantities between the solid and liquid states, and ΔH_d is accompanied with various changes in the states: mainly, (1) the breaking down of the crystal structure, and the dedimerization of the solute molecules which is related to the dissociation ratio, (2) the breaking of the interaction between the solvent molecules, (3) the formation of the interaction between the solute and the solvent molecules.

For the comparison of ΔH_d between C14—18, the heat of breaking the interaction between the ethanol molecules can be eliminated from consideration because this process is common to C14—18. Also, the dissociation ratio (α) can be eliminated from consideration because α of FA in ethanol is 100%.[15]

ΔH_d was plotted against n, and shown in Fig. 1(a). As can be seen in Fig. 1, ΔH_d increased linearly with increasing n. The increment in ΔH_d of FA as a function of the number of methylene groups (–CH$_2$–) in the alkyl chain is obtained as 4.40±0.10 kJ (mol –CH$_2$–)$^{-1}$ from the slope of the straight line shown in Fig. 1(a). Assuming a negligible heat of mixing (ΔH_m) for the FA-ethanol solutions, the rate of change of ΔH_d with varying n of FA allows an estimate to be made of the increment in the latent heat of fusion of FA as a function of the number of (–CH$_2$–).

The value of 4.40±0.10 kJ (mol –CH$_2$–)$^{-1}$ is in good agreement with the value[7] of 4.40±0.20 kJ (mol –CH$_2$–)$^{-1}$ obtained for even-numbered FA in benzene. In addition, the (CH$_2$)-increments have been obtained as 4.6 kJ (mol –CH$_2$–)$^{-1}$ for methyl alkanoate in trichloromethane[17] and 4.2 kJ (mol –CH$_2$–)$^{-1}$ for 1-alkanol in water.[18]

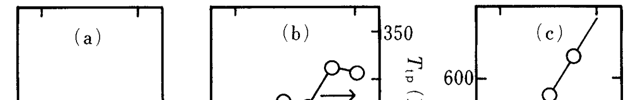

Fig. 1. Thermodynamic Properties of *n*-Fatty Acids

(a) heats of dissolution, ΔH_d, in ethanol. (b) heats of fusion,[1b,c] ΔH_f, and triple-point temperatures,[1b,c] T_{tp}. (c) molar heat capacities,[1b,c] C_p. Temperature: 215 K, ●; 310 K, ◑; 345 K, ○. C14—18 are in solid states at 215 and 310 K and in liquid states at 345 K.

The plots of ΔH_d in ethanol against n indicated a single line pattern as can be seen in Fig. 1(a), and did not indicate a zig-zag pattern as can be seen in the relationship between the mp and n. A similar phenomenon is found for 1-alkanols.[18]

Comparison of ΔH_d with ΔH_f and C_p Fusion is the phenomenon that a solid state changes into a liquid state, and the fusion of FA is accompanied with a partial dissociation of FA. Namely, the fusion of FA is represented schematically as follows:

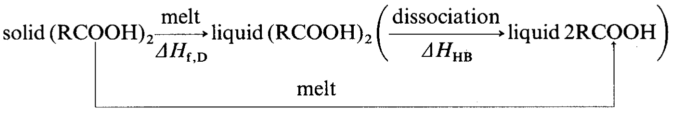

Chart 2

where ΔH_{HB} is the heat of dissociation.

In contrast to this ΔH_d and ΔH_f are of differential thermal quantities, and C_p is a thermal quantity in a certain state.

The values of ΔH_f have been obtained as follows: 44.7 kJ mol^{-1} [1a] and 45.1 kJ mol^{-1} [1c] for C14, 41.5 kJ mol^{-1} [1b] and 42.1 kJ mol^{-1} [1a] for C15, 53.4 kJ mol^{-1} [1a] and53.7 kJ mol^{-1} [1c] for C16, 51.3 kJ mol^{-1} [1b] and 51.5 kJ mol^{-1} [1a] for C17, and 61.2 kJ mol^{-1},[1c] 62.5 kJ mol^{-1},[3] 62.6 kJ mol^{-1} [6a] and 63.0 kJ mol^{-1} [1a] for C18. The values of ΔH_d are larger than these values of ΔH_f. This is a phenomenon commonly found. FA exist as dimer-form in the solid state[14] and exist almost as dimer-form in the liquid state.[16] It has been reported[19] that C18 is dissociated in the melt at the mp to 1.3%. On the contrary, C18 is dissociated in the dissolution in methanol to 100%,[6a] and it is considered that C18 is dissociated to 100% in ethanol. The value of ΔH_{HB} is reported as 56 kJ mol^{-1} for C18.[19] It is, therefore, understood that the values of ΔH_d are larger than those of ΔH_f. Furthermore, the relationship between ΔH_d and ΔH_f are represented as follows:

$$\Delta H_d = \Delta H_f + \Delta C_p(T - T_f) + \Delta H^E \qquad (1)$$

where ΔC_p is the difference in the heat capacities between the solid and liquid, ΔH^E is the excess enthalpy, T and T_f are the temperatures of the solution and fusion, respectively. In the second term on the right hand side in Eq. 1, the values of ΔC_p and $\Delta C_p(T - T_f)$ are 0.02—0.1 kJ K^{-1} mol^{-1} and −0.3—−3 kJ mol^{-1}, respectively, for C14—18. Taking the value of $\Delta C_p(T - T_f)$ into account, the value of ΔH^E is estimated as 16—20 kJ mol^{-1} for even-numbered FA and 25—27 kJ mol^{-1} for odd-numbered FA. The values of $\Delta C_p(T - T_f)$ are small, so Eq. 1 may possibly be simplified as follows:

$$\Delta H_d \fallingdotseq \Delta H_f + \Delta H^E \qquad (2)$$

ΔH^E relates generally to ΔH_{HB} and the heat of mixing (ΔH_m). The value of ΔH_m in general is 10—100 J mol^{-1} for a binary system of an aliphatic acid and an aliphatic alcohol,[20] and the value of ΔH_m for the binary system of ethanol and ethyl octadecanoate at 310.15 K has been reported as 0.4—1.7

kJ mol^{-1} at various mole fractions.[21)] In addition, the heat of the dipole–dipole interactions of COOH and OH is less than 1 kJ mol^{-1}.[6a)] The value of ΔH_m is small, so it is suggested that ΔH^E depends mainly on ΔH_{HB}.

The difference between ΔH_d in ethanol and ΔH_f[3)] of C18 is $(79.1-62.5=16.6)$ kJ mol^{-1}. In case decane[6a)] is used for the dissolution of C18, the difference is $(70.6-62.5=8.1)$ kJ mol^{-1}: the difference being smaller by a partial dissociation than that for the case of ethanol.

We are interested in the so called odd-even effect so the values[1b,c)] of ΔH_f were plotted against n and shown in Fig. 1(b). As can be seen in Fig. 1(b), the plots of ΔH_f *vs.* n indicated a zig-zag pattern which indicates an upward convex at even-numbered positions. The zig-zag line can be separated by two individual lines among FA with the even carbon number and the odd carbon number drawn by two dotted lines as in Fig. 1(b). The upper line is for even-numbered FA and the lower one for odd-numbered FA. The $(CH_2)_2$-increments of ΔH_f are obtained from the slope of each dotted line as 8.52 and 8.76 kJ (mol $-(CH_2)_2-)^{-1}$ for even- and odd-numbered FA, respectively, indicating them nearly equal to the value of 4.40 ± 0.10 kJ (mol $-CH_2-)^{-1}$ for the (CH_2)-increment of ΔH_d.

The triple point temperatures (T_{tp})[1b,c)] of FA were plotted against n and shown in Fig. 1(b) together with the values of ΔH_f. The relationship between T_{tp} and n indicates a zig-zag pattern which indicates an upward convex at even-numbered positions. It is evident that ΔH_f relates closely to T_{tp}.

It is very interesting that the plots of ΔH_d *vs.* n indicate a single line pattern, although those of ΔH_f *vs.* n indicate a zig-zag pattern. This means that ΔH^E in Eq. 2 for the dissolution of odd-numbered FA is larger than that for the dissolution of even-numbered FA. In addition, this may lead to a suggestion that the difference in ΔH^E between odd- and even-numbered FA is mainly caused by ΔH_{HB} because ΔH_m is small enough to be neglected as mentioned above. However, even- and odd-numbered FA are dissociated to 100% in ethanol, and the dissociation ratio (α) of C18 in the melt has a very small value[19)] of 1.3%. It is, therefore, considered that ΔH_{HB} does not have a strong enough influence to transform a zig-zag pattern into a single line pattern even if there is a small difference in α between even- and odd-numbered FA. Therefore, the heat of transition (ΔH_t) may be concerned in the difference in ΔH^E. The values of ΔH_t were reported as 7.30 kJ mol^{-1} [1a)] and 8.12 kJ mol^{-1} [1b)] for C15 and 7.30 kJ mol^{-1} [1a)] and 7.44 kJ mol^{-1} [1b)] for C17. It was reported by Schaake *et al.*[1c)] that the relationship between ΔH_f for even-numbered FA and the sum of ΔH_f and ΔH_t for odd-numbered FA indicates a single line pattern against n, although the interpretation was not made.

The relationship between ΔH_d of FA in ethanol and n indicated a single line pattern. It is considered that the single line pattern is not always obtained for all solvents, especially for the solvents in which a complete dissociation of FA is not followed, because $\Delta H_{d,M}$ and $\Delta H_{d,D}$ shown in Chart 1 and the dissociation ratio are strongly solvent dependent as observed by Lai and Kertes.[10)]

Next, the values[1b,c)] of C_p for C14—18 at three points of temperature, where FA are in the solid state at 215 and 310 K and in the liquid state at 345 K, were plotted against n and shown in Fig. 1(c).

C_p of the liquid acids between the T_{tp} and 20 K above T_{tp} was formulated by Schaake *et al.*[1c)] as follows:

$$C_p=A_0+A_1n+A_2(T-T_{tp}) \tag{3}$$

where $A_0=-10.8\pm1.1$ and -2.5 ± 1.3 J K^{-1} mol^{-1}, $A_1=36.47\pm0.07$ and 36.32 ± 0.09 J K^{-1} mol^{-1}, and $A_2=0.71\pm0.04$ and 0.65 ± 0.03 J K^{-2} mol^{-1}, for odd- and even-numbered FA, respectively. These coefficients indicate that there is an odd-even effect in C_p for the alkanoic acids in the liquid state. Therefore, the plots of C_p *vs.* n should exactly indicate a zig-zag pattern. However, the odd-even effect is too small to recognize a zig-zag pattern as is indicated by open circles in Fig. 1(c) for FA in the liquid state at 345 K. C_p of the solid acids has not been formulated by Schaake *et al.*[1c)] However, the plots of C_p of the solid acids at 215 K against n are slightly recognized as a zig-zag pattern which indicates an upward convex at even-numbered positions between $n=7$—13, while the relationship between C_p and n is regarded as linear for $n\geqq14$ as is indicated by closed circles in Fig. 1(c). According to the judgements on the single line pattern for ΔH_d and the zig-zag pattern for ΔH_f, it is mentioned that the relationship between C_p and n is a single line pattern at least $n\geqq14$. Near the transition temperature for each FA, larger deviations were found in Table reported by Schaake *et al.*[1b,c)] Still the single line pattern for the plots of C_p *vs.* n is obtained at 310 K where ΔH_d is measured, although the deviation from the line is larger than that for the other two cases. As can be seen in Fig. 1(c) at least for C14—18, C_p increased linearly with increasing n for all cases of the solid and liquid states at below and above the mp, and C_p was irrespective of even- or odd-numbered FA.

There is an odd-even effect in ΔH_f, while there is not an odd-even effect in ΔH_d. It was found that ΔH_d of FA in ethanol, in which a complete dissociation is accompanied, indicates a similar tendency as the relationship between C_p and n.

Conclusion

No concentration dependency on ΔH_d of FA in ethanol was found within the concentration ranges of at least 1×10^{-3}—2×10^{-2} mol dm^{-3}. ΔH_d increased linearly with increasing n, and (CH_2)-increment was obtained as 4.40 ± 0.10 kJ mol^{-1}. The plots of ΔH_d *vs.* n indicated a single line pattern and the so called odd-even effect was not found, while the plots of ΔH_f *vs.* n indicated a zig-zag pattern. ΔH_d was larger than ΔH_f, and the difference between ΔH_d and ΔH_f for odd-numbered FA was larger than that for even-numbered FA.

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