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Dissolution States of Normal Alkane Derivatives with a Polar Group in Water

Nobuo Nishino, Satoshi Morimoto,† and Masao Nakamura*
Department of Chemistry, Faculty of Science, Tokai University, 1117 Kitakaname, Hiratsuka 259-12
†Research Institute for Polymers and Textiles, 1-1-4 Yatabe-Higashi, Tsukuba 305
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This paper proposes a method by means of which the heat of solution at an infinite dilution of an organic compound in water, directly measured by means of calorimetry at a given temperature, is extended over a wide range of temperatures by the use of a phase diagram with water. The heat of solution at an infinite dilution in water over a temperature range from 290 to 350 K, which is estimated by this method for some alkanols and alkanoic acids, increases with a rise in the temperature and has a transition temperature from the exothermic region to the endothermic region which is close to the minimum dissolution temperature in the solubility curve in water for each substance. The increase in the heat of solution might be due to the breakdown of the iceberg formed around the alkyl group. The difference between the partial molar heat capacity at an infinite dilution and the molar heat capacity at the pure state, $\Delta_s c_{p2}^\infty$, has its maximum at a certain temperature. The higher homolog shows a sharper curve with a lower maximum temperature. The curve of $\Delta_s c_{p2}^\infty$ *vs.* the temperature for 2- or 3-alkanol corresponds to that for the lower 1-alkanol. These facts reveal that a polar group, such as OH and COOH, would preferentially break the weaker structure of the iceberg within its breaking sphere, which structure should break down at a lower temperature.

In previous papers,[1,2] the present authors have constructed phase diagrams for binary systems of water and normal alkane derivatives, such as alkanols, alkylamines, and alkanoic acids, in which each aqueous-phase line commonly has a minimum point at a temperature, but in which the corresponding organic-phase line is monotonical. Such phenomena suggest that the state of the aqueous phase changes with the temperature, while those of the organic phases do not change so much. It is now believed that an ice-like structure of water, referred to as an "iceberg," is formed around a dissolved nonpolar alkyl group, but gradually breaks down with a rise in the temperature.[3] If this is true, the partial molar enthalpy of such a solute in water should increase with a rise in the temperature. The change in the partial molar enthalpy of a solute with the temperature must be reflected by the change in the heat of solution, since the heat of evaporation is almost independent of the temperature for such substances.[1] It has been shown that the heat of solution at an infinite dilution, $\Delta_s h_2^\infty$ can be evaluated correctly from the phase diagram and the activity coefficient of the organic substance in its own phase, γ_2^{or}, according to the following equation, when the solubility of the organic substance in water is so small that the aqueous phase may be regarded as an ideal dilute solution:[2]

$$\Delta_s h_2^\infty = R\left[\frac{\partial \ln (x_2^{\mathrm{or}}\gamma_2^{\mathrm{or}}/x_2^{\mathrm{aq}})}{\partial T^{-1}}\right]_{p,\mathrm{sat}}, \tag{1}$$

where x_2^{or} and x_2^{aq} are the mole fractions of an organic substance in organic and aqueous phases at mutual saturation respectively; T, the absolute temperature, p, the pressure, and R, the gas constant, and where "sat" designates mutual saturation. Unfortunately, γ_2^{or} is available for only a few substances in the literature.[4,5]

The following approach, however, can be used instead of measurements of γ_2^{or} to evaluate $\Delta_s h_2^\infty$ over a wide range of temperatures. When mutual saturation is maintained under a constant pressure, the differential of ln γ_2^{or} with respect to the reciprocal of the absolute temperature, T^{-1}, can be expressed by:

$$\left[\frac{\partial \ln \gamma_2^{\mathrm{or}}}{\partial T^{-1}}\right]_{p,\mathrm{sat}} = \left[\frac{\partial \ln \gamma_2^{\mathrm{or}}}{\partial \ln x_2^{\mathrm{or}}}\right]_{T,p}\left[\frac{\partial \ln x_2^{\mathrm{or}}}{\partial T^{-1}}\right]_{p,\mathrm{sat}} + \left[\frac{\partial \ln \gamma_2^{\mathrm{or}}}{\partial T^{-1}}\right]_{p,x_2^{\mathrm{or}}}, \tag{2}$$

because γ_2^{or} is, in general, a function of T, p, and x_2^{or}. The partial pressures of 1-propanol over its mixtures with water at several temperatures are available in the literature;[4] the literature shows that the estimated activity coefficients of 1-propanol are not so dependent on the temperature as on the composition, as is shown in Fig. 1. If $[\partial \ln\gamma_2^{\mathrm{or}}/\partial T^{-1}]_{p,x_2^{\mathrm{or}}}$, therefore, is assumed to be negligible in comparison with the first term, Eq. 2 is reduced to:

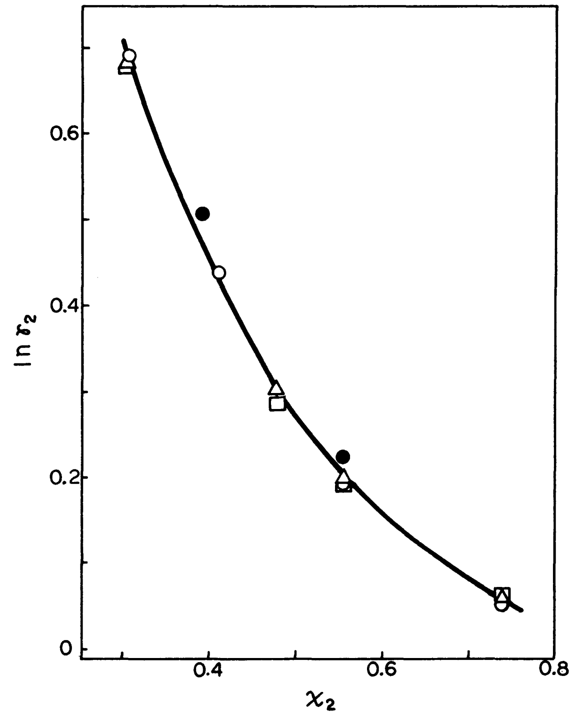

Fig. 1. Plots of the activity coefficient of 1-propanol in the mixture with water *vs.* the mole fraction of 1-propanol calculated from the vapor pressures.[4]
●: 303.50 K, ○: 323.07 K, △: 339.09 K, □: 353.95 K.

$$\left[\frac{\partial \ln \gamma_2^{\mathrm{or}}}{\partial T^{-1}}\right]_{p,\mathrm{sat}} = \left[\frac{\partial \ln \gamma_2^{\mathrm{or}}}{\partial \ln x_2^{\mathrm{or}}}\right]_{T,p}\left[\frac{\partial \ln x_2^{\mathrm{or}}}{\partial T^{-1}}\right]_{p,\mathrm{sat}}. \qquad (3)$$

The substitution of Eq. 3 into Eq. 1 gives:

$$\Delta_s h_2^\ominus = R\left[\frac{\partial \ln \gamma_2^{\mathrm{or}}}{\partial \ln x_2^{\mathrm{or}}}\right]_{T,p}\left[\frac{\partial \ln x_2^{\mathrm{or}}}{\partial T^{-1}}\right]_{p,\mathrm{sat}} + R\left[\frac{\partial \ln (x_2^{\mathrm{or}}/x_2^{\mathrm{aq}})}{\partial T^{-1}}\right]_{p,\mathrm{sat}}. \qquad (4)$$

If $\Delta_s h_2^\ominus$ is actually determined at a certain temperature besides the phase diagram, then $[\partial \ln \gamma_2^{\mathrm{or}}/\partial \ln x_2^{\mathrm{or}}]_{T,p}$ at that temperature can be obtained by the aid of Eq. 4. The values for $\Delta_s h_2^\ominus$ at other temperatures may now be estimated, if $[\partial \ln \gamma_2^{\mathrm{or}}/\partial \ln x_2^{\mathrm{or}}]_{T,p}$ is assumed to be independent of the temperature. The solubility of water in an organic phase, $(1-x_2^{\mathrm{or}})$, does not change very markedly between 290 and 350 K.[2] The heats of solution at an infinite dilution, $\Delta_s h_2^\ominus$, have been measured calorimetrically at 298 or 303 K for several compounds.[6–12] The purpose of the present paper is to determine the dependence of $\Delta_s h_2^\ominus$ on the temperature as exactly as possible, in order to elucidate the dissolution states of normal alkane derivatives with a polar group in water over a wide range of temperatures, including the change in the iceberg formed around the alkyl groups.

Experimental

The alkanols and alkanoice acids used were the same as those described in a previous paper.[1] They were used after having been dried over calcium hydride and were above 99.9% in purity, as verified by gas chromatography using a Shimadzu GC-4CM PF apparatus.

Measurements were made of the heats of mixing various amounts of a solute with a constant amount of water, 5.55 mol, at 298 K by using a 8721-1 solution calorimeter of the precision calorimetry system (LKB Produkter AB), according to a procedure described elsewhere.[13]

Results and Discussion

Temperature Dependence of the Heat of Solution at an Infinite Dilution. Figure 2 shows that the heats of mixing, ΔH, of normal alkane derivatives with water, measured at 298 K, are proportional to the number of moles of the normal alkane derivative added, n_2, while the amount of water is always constant, 5.55 mol. This means that the solutions are dilute enough to be regarded as ideal dilute solutions; therefore, the slope of each straight line is equal to the heat of solution at an infinite dilution, $\Delta_s h_2^\ominus$ for each substance.[14] The values for $\Delta_s h_2^\ominus$ obtained are summarized in Table 1, together with the values from the literature.[7,11] The value of −8.24±0.08 kJ mol⁻¹ for 1-pentanol can be compared with that of −8.08±0.42 kJ mol⁻¹ measured by Aveyard and Mitchell,[7] which is closer than those obtained by other authors.[6,8,9] The values of $[\partial \ln \gamma_2^{\mathrm{or}}/\partial \ln x_2^{\mathrm{or}}]_{T,p}$ are also listed in Table 1; they were estimated from the $\Delta_s h_2^\ominus$ values in Table 1 and the phase diagrams with water,[2] according to Eq. 4. The value for 1-butanol, −1.09, is comparable to that of −1.01 estimated from

Table 1. Heats of solution at infinite dilution and $[\partial \ln \gamma_2^{\mathrm{or}}/\partial \ln x_2^{\mathrm{or}}]_{T,p}$ of normal alkane derivatives in water at 298 K

Substance	$\Delta_s h_2^\ominus$ / kJ mol⁻¹	$\left[\frac{\partial \ln \gamma_2^{\mathrm{or}}}{\partial \ln x_2^{\mathrm{or}}}\right]_{T,p}$
1-Butanol	−9.00±0.42[a]	−1.09
1-Pentanol	−8.24±0.08	−1.30
1-Hexanol	−5.77±0.42[a]	−1.31
2-Pentanol	−11.82±0.08	−0.65
2-Hexanol	−10.81±0.05	−0.55
2-Heptanol	−9.62±0.14	−1.04
3-Pentanol	−12.80±0.08[b]	−0.79
3-Hexanol	−12.59±0.46[b]	−1.75
Pentanoic acid	−0.50±0.21[a]	−0.72
Hexanoic acid	0.92±0.42[a]	−0.74

a) Ref. 7. b) Ref. 11.

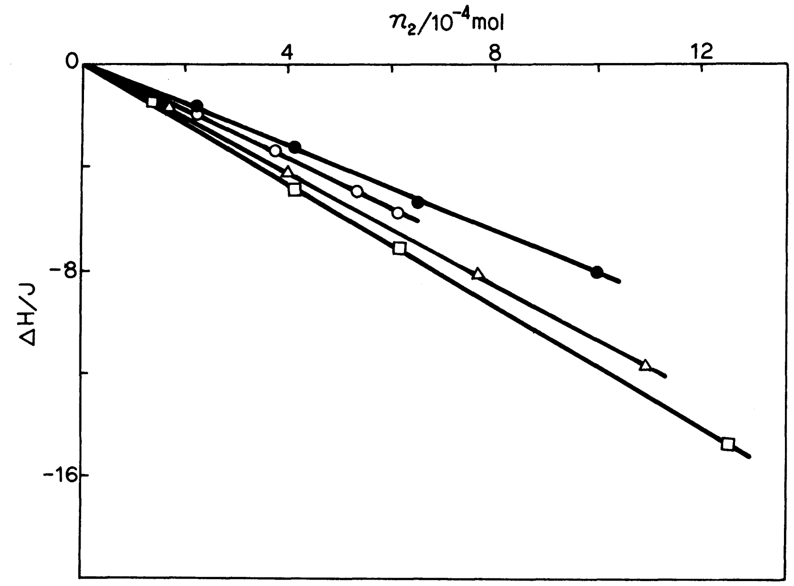

Fig. 2. Heat of mixing of n_2 mol of normal alkane derivatives with 5.55 mol of water at 298 K.
●: 1-Pentanol, □: 2-pentanol, △: 2-hexanol, ○: 2-heptanol.

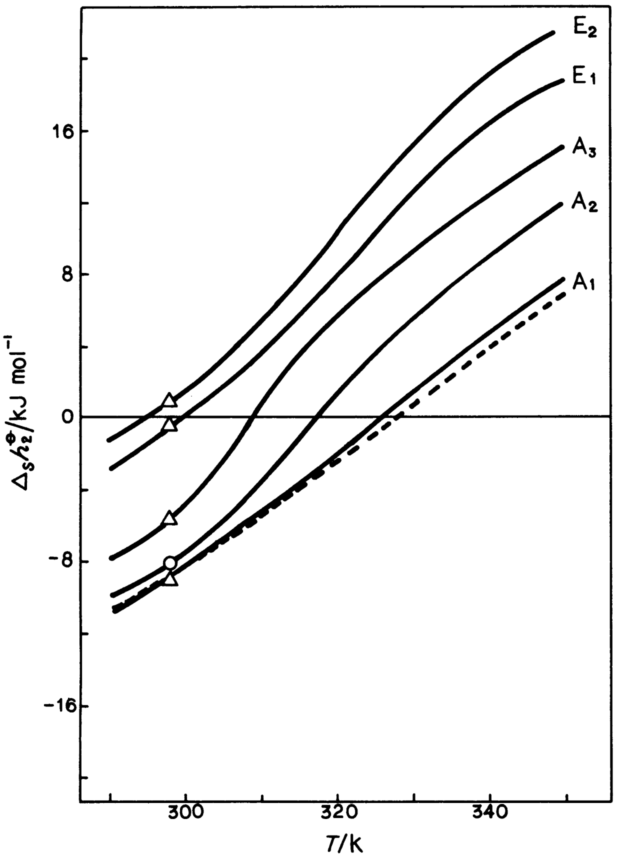

Fig. 3. Heat of solution at an infinite dilution *vs.* temperature for 1-alkanols and alkanoic acids.
A_1: 1-Butanol, A_2: 1-pentanol, A_3: 1-hexanol, E_1: pentanoic acid, E_2: hexanoic acid.
○ and △ are directly measured by calorimetry (○: obtained here, △: from the literature.) Dotted line is obtained by substituting γ_2^{or} of 1-butanol5) into Eq. 4.

the partial vapor pressures at 298 K.5) The heats of solution at an infinite dilution, $\Delta_s h_2^\ominus$ at other temperatures were estimated from the value of $[\partial \ln \gamma_2^{or}/\partial \ln x_2^{or}]_{T,p}$ in Table 1 and the phase diagram,2) again by the aid of Eq. 4, assuming $[\partial \ln \gamma_2^{or}/\partial \ln x_2^{or}]_{T,p}$ to be constant over the range of temperatures in which the phase diagram was measured. The values of $\Delta_s h_2^\ominus$ thus obtained are plotted against the temperature in Figs. 3 and 4, in which ○ and △ are directly measured by means of calorimetry. Butler *et al.* have obtained the activity coefficient of 1-butanol, γ_2^{or}, over a wide range of compositions with water at 298 K by the determination of the partial vapor pressure.5) The values of $\Delta_s h_2^\ominus$ obtained from γ_2^{or} and the phase diagram by the use of Eq. 4, superimposed as a dotted line in Fig. 3, are substantially coincident with the line, A_1, estimated by the present method over the whole range of temperatures.

The heat of solution at an infinite dilution, $\Delta_s h_2^\ominus$ increases with a rise in the temperature, from negative to positive, for each substance. Thus, there is a transition temperature, T_t, from the exothermic region to the endothermic region, *i.e.*, the temperature at which $\Delta_s h_2^\ominus=0$. The transition temperature, T_t, is close to the minimum dissolution temperature, T_m, on the solubility curve of the substance in water,1) within the difference between 0.5 and 6.3 K.

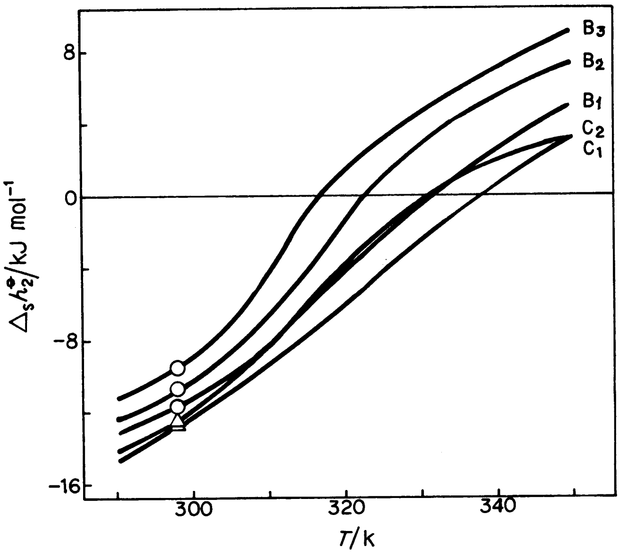

Fig. 4. Heat of solution at an infinite dilution *vs.* temperature for 2- and 3-alkanols in water.
B_1: 2-Pentanol, B_2: 2-hexanol, B_3: 2-heptanol, C_1: 3-pentanol, C_2: hexanol, ○ and △ are directly measured by calorimetry. (○: obtained here, △: from the literature)

The Breakdown of the Iceberg with the Temperature. The increase in the heat of solution at an infinite dilution, $\Delta_s h_2^\ominus$, with the temperature, as shown in Figs. 3 and 4, may be attributed mainly to the increase in the partial molar enthalpy of the solute at an infinite dilution in the aqueous solution, since the heat of evaporation is almost independent of the temperature.1) When an organic molecule with a hydrophobic group, such as an alkyl group, is introduced in water, the water molecules in the vicinity of the dissolved hydrophobic group form a so-called iceberg, which gradually breaks down with the subsequent rise in the temperature.3) Such phenomena should make the partial molar enthalpy of the solute higher with the temperature.

The tangent of the curve in Figs. 3 and 4 is equal to the difference between the partial molar heat capacity of the solute at an infinite dilution and its molar heat capacity at the pure state, $\Delta_s c_{p2}^\ominus$. The relations between $\Delta_s c_{p2}^\ominus$ and the temperature are shown in Figs. 5, 6, 7, and 8 for each homologous series; all the curves are characterized as having a maximum at a certain temperature, T_x. The curves reveal that most of the water molecules in the iceberg break down around T_x and reinforce the concept that the iceberg structure disappears at a higher temperature.15,16) The higher homolog shows a sharper curve with a lower T_x in any series. The curve for 2- or 3-alkanol in Figs. 6 and 7 corresponds to that for the lower 1-alkanol in Fig. 5. These facts suggest that there are structures different in strength in an iceberg around an alkyl group; the weaker one breaks down at the lower temperature, and a polar group, such as OH or COOH, acts as a breaker against the iceberg,17) preferentially the weaker structure, which should break down at the lower temperature. If a polar group is assumed to have a certain breaking sphere, the number of water molecules in an iceberg within the sphere would be more for 2- or 3-alkanol than for 1-alkanol. Thus, it may

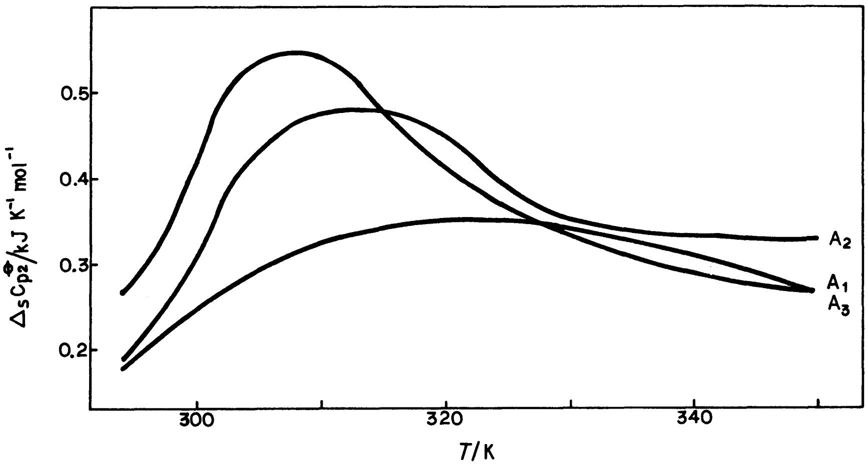

Fig. 5. The difference between the partial molar heat capacity at an infinite dilution in water and the molar heat capacity at the pure state for 1-alkanols.
A_1: 1-Butanol, A_2: 1-pentanol, A_3: 1-hexanol.

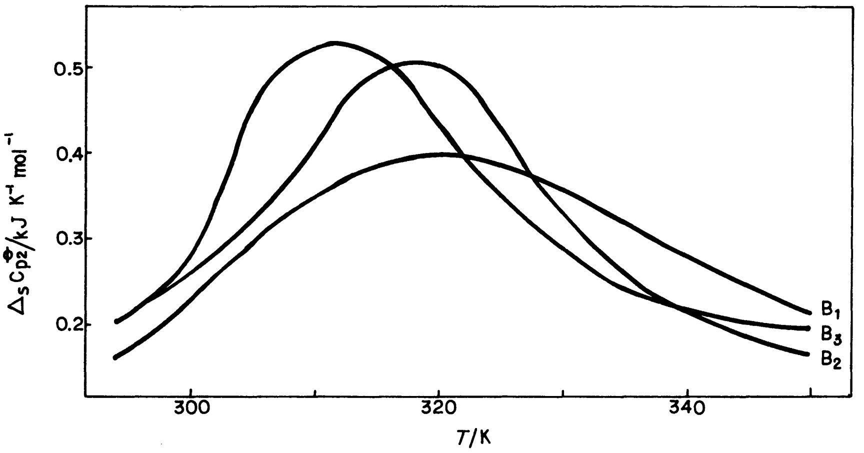

Fig. 6. The difference between the partial molar heat capacity at an infinite dilution in water and the molar heat capacity at the pure state for 2-alkanols. B_1: 2-Pentanol, B_2: 2-hexanol, B_3: 1-heptanol.

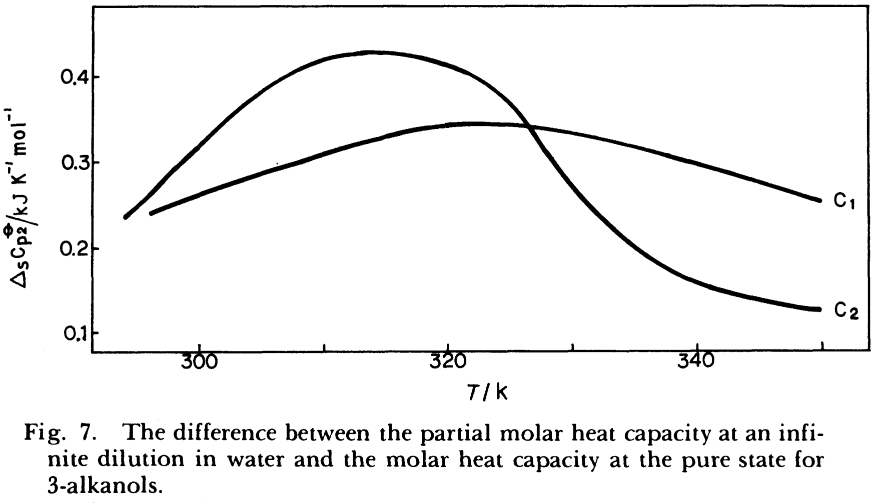

Fig. 7. The difference between the partial molar heat capacity at an infinite dilution in water and the molar heat capacity at the pure state for 3-alkanols.
C_1: 3-Pentanol, C_2: 1-hexanol.

be concluded that a polar group breaks the weaker structure of the iceberg within its breaking sphere. In addition, the COOH group must be a stronger breaker than the OH group, because the curves for alkanoic acids in Fig. 8 are broader curves, with higher T_x values, than the corresponding curves for 1-alkanols in Fig. 5.

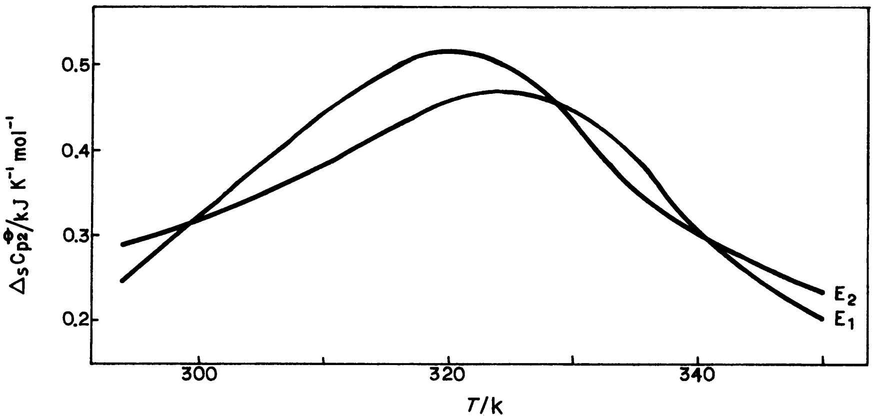

Fig. 8. The difference between the partial molar heat capacity at an infinite dilution in water and the molar heat capacity at the pure state for alkanoic acids.
E_1: Pentanoic acid, E_2: hexanoic acid.

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