

YU ISSN 0011-1643

UDC 541.18.041.5

CCA-1985

Original Scientific Paper

Thermochemistry of Precipitation of Alkaline Earth Laurates

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Received July 5, 1990

The solubility of alkaline earth laurates was studied in aqueous solutions as a function of temperature. Dissolution enthalpies $\Delta_d H^\circ$, determined directly by calorimetry, were compared with the solubility data. The enthalpy change $\Delta_d H^\circ$ showed linear dependence on temperature. The heat capacity change $\Delta_d C_p$, calculated from $\Delta_d H^\circ$ vs. T plot, was found to be $1.1 \text{ kJ mol}^{-1} \text{ K}^{-1}$ for all salts.

The entropy change of dissolution $\Delta_d S^\circ$, as obtained from solubility and calorimetry, showed linear dependence on $\ln T$; $\Delta_d C_p$, calculated from these plots, was the same as obtained from temperature dependence of the enthalpy.

Specific behaviour of each alkaline earth cation is characterized by the entropy change $\Delta_d S^\circ$, which is the lowest for calcium salt, thus explaining the irregular low solubility of calcium carboxylates. The so called compensation effect was explained in terms of the »critical compensation temperature«, which was found to be just an average temperature within the examined temperature region.

INTRODUCTION

The enthalpy of dissolution ($\Delta_d H^\circ$) of ionic surfactants has mostly been obtained from solubility data¹⁻¹⁰, assuming that $\Delta_d H^\circ$ and $\Delta_d S^\circ$ (the entropy of dissolution) are independent of temperature, *i.e.* a negligible heat capacity change of dissolution ($\Delta_d C_p \approx 0$).

Calorimetric measurements of precipitation heats of several ionic surfactants showed that enthalpy depended significantly on temperature.¹¹⁻¹⁴ A linear relationship between enthalpy and thermodynamic temperature was observed, from which $\Delta_d C_p$ was evaluated. The true values of thermodynamic parameters ($\Delta_d H^\circ(T_0)$, $\Delta_d S^\circ(T_0)$ and $\Delta_d C_p$) can be evaluated by using both solubility and calorimetric data.

This article reports thermodynamic parameters of various alkaline-earth salts of lauric acid as obtained by calorimetry and solubility measurements.

EXPERIMENTAL

Materials

Analytically pure magnesium, calcium and strontium nitrates («Kemika», Zagreb) and barium nitrate («Merck», Darmstadt) were used. The salts were dissolved in doubly distilled water and standardized by complexometric titration. Sodium laurate was prepared by neutralization of lauric acid (FLUKA, puriss.) with sodium hydroxide, free of carbon dioxide, to pH \approx 10. At this pH value, dissociation of lauric acid is practically complete.

Methods

The solubility of laurate salts was determined by mixing the reacting components (alkaline earth nitrates and sodium laurate), as described earlier.⁵ The appearance of solid phase was examined by the scattering method, using the Virtis Brice Phoenix universal light scattering photometer, model DU 2000.

A Fisher glass electrode was used for pH measurements in combination with the Orion ROSS reference electrode. Standard buffer solutions were prepared according to reference 15.

Reaction enthalpies were measured by means of the isoperibolic reaction calorimeter constructed by Simeon *et al.*¹⁶ The reaction vessel contained 70 cm³ of lauric acid solution (2×10^{-3} mol dm⁻³) dissolved in sodium hydroxide (2.2×10^{-3} mol dm⁻³). Small volumes (0.5 cm⁻³) of metal nitrate solutions (0.1 mol dm⁻³) were introduced into the reaction vessel by means of a microburette.

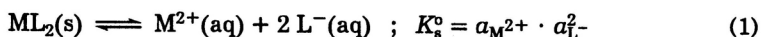
The crystal structure of calcium laurate was examined using an X-ray powder diffractometer. The samples were prepared at 20 and 50 °C. Some measurements were performed with crystals dispersed in the mother liquid while others were dried at the same temperatures. Due to limitations of the instrument, the X-ray analysis was carried out at room temperature. Since the duration of these measurements was relatively short, no structural changes were assumed.

INTERPRETATION OF DATA

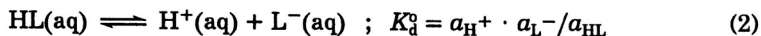
Solubility

The solubility equilibria of alkaline earth laurates at different temperatures are characterized by the equilibrium constant of dissolution K_s^0 . These values were calculated for each solubility experiment by an iterative procedure⁵ taking into account the following equilibria:

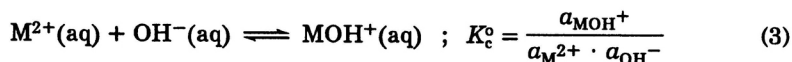
– crystal dissolution:



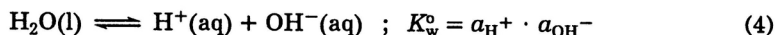
– acid dissociation:



– complex formation:



– water dissociation:



M^{2+} and L^- denote alkaline earth cation and laurate ion, respectively, while a is ionic activity. The value of a_{H^+} is taken as $10^{-\text{pH}}$. In the investigated pH region (6–8), no precipitation of lauric acid was observed, as tested by separate experiments. No association (ion pairing) of alkaline earth laurates was evidenced, contrary to what was observed with the silver laurate⁵ or thallium oleate¹⁷.

The activity coefficients γ_i were obtained from:

$$\lg \gamma_i = -z^2 A I_c^{1/2} / (1 + I_c^{1/2}) \quad (5)$$

where A is the Debye-Hückel constant taken from literature.¹⁵

The ionic strength I_c was calculated from:

$$\begin{aligned} I_c &= (c_{\text{Na}^+} + c_{\text{NO}_3^-} + c_{\text{OH}^-} + c_{\text{H}^+} + 4c_{\text{M}^{2+}} + c_{\text{L}^-} + c_{\text{MOH}^+})/2 \approx \\ &\approx (2[\text{M}(\text{NO}_3)_2]_{\text{tot}} + [\text{NaOH}]_{\text{tot}} + 4c_{\text{M}^{2+}} + c_{\text{L}^-})/2 \end{aligned} \quad (6)$$

Equation (5) is valid below $I_c = 0.1 \text{ mol dm}^{-3}$, which was always satisfied. The second part of Eq. (6) is an applicable approximation since the concentrations of H^+ , OH^- and MOH^+ ionic species were always negligible. For example, the concentration of MOH^+ was in all experiments below $10^{-6} \text{ mol dm}^{-3}$, which is several orders of magnitude smaller than I_c . The total concentration of lauric acid in the absence of precipitate is:

$$[\text{HL}]_{\text{tot}} = c_{\text{L}^-} + c_{\text{HL}} \quad (7)$$

and the total concentration of metal ions is:

$$[\text{M}(\text{NO}_3)_2]_{\text{tot}} = c_{\text{M}^{2+}} + c_{\text{MOH}^+} \quad (8)$$

The total concentration of sodium hydroxide was adjusted to the excess over HL:

$$[\text{NaOH}]_{\text{tot}} = 1.1 [\text{HL}]_{\text{tot}} \quad (9)$$

The equilibrium constant K_s° was calculated from each experimental point (Figures 1 and 2) via Eq. (10) which was derived from Eqs (1) to (9)

$$K_s^\circ = \frac{\gamma [\text{M}(\text{NO}_3)_2]_{\text{tot}} \times [\text{HL}]_{\text{tot}}^2}{(K_w^\circ / 10^{-\text{pH}} + 1/\gamma^3) (1/\gamma + 10^{-\text{pH}}/K_3) ^2} \quad (10)$$

Total concentrations $[\text{M}(\text{NO}_3)_2]_{\text{tot}}$, $[\text{HL}]_{\text{tot}}$ were predetermined, while pH values were measured after the equilibration. The activity coefficient γ corresponds to univalent ions and was calculated by Eq. (5). The dissociation constant of lauric acid (K_3°)

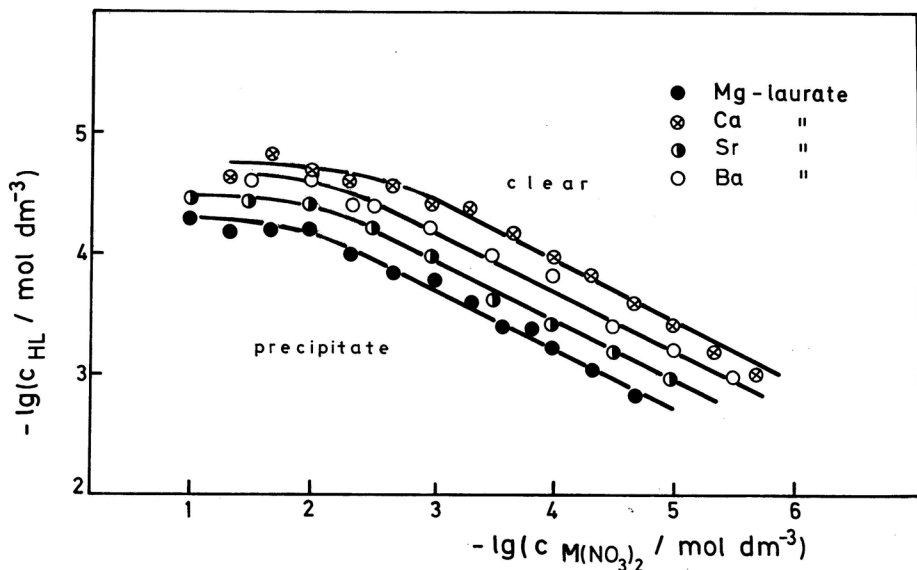


Figure 1. Solubility boundaries for Mg, Ca, Sr and Ba-laurates, determined by light scattering at 20 °C.

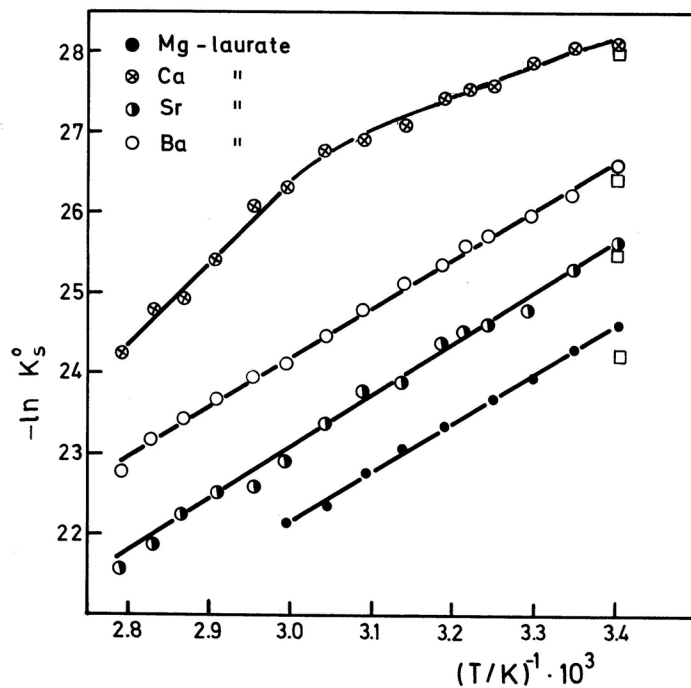


Figure 2. Solubility of Mg, Ca, Sr and Ba-laurates (expressed as $\ln K_s^0$) as a function of thermodynamic temperature. The squares denote literature values.²⁰

at 20 °C was taken from literature.¹⁸ At higher temperatures, K_d^o was estimated by using the value at 20 °C and the dissociation enthalpy of acetic acid.¹⁹ The latter approximation is applicable since the uncertainty in K_d^o value had practically no influence on the calculated K_s^o values. The equilibrium constants of MOH^+ formation (K^o) at different temperatures were taken from literature.¹⁹

Calorimetry

The dissolution enthalpy $\Delta_d H^o$ was obtained from the measured heat of precipitation and the extent of the precipitation reaction. The latter was calculated from the initial amounts of reactants by considering the equilibria described by Eqs. (1–4). Total concentrations of the reactants in calorimetric experiments were chosen so that the extents of reactions other than the precipitation one were negligible.

The equilibrium constant is related to the standard dissolution entropy and enthalpy as follows:

$$-RT \ln K_s^o(T) = \Delta_d G^o(T) = \Delta_d H^o(T) - T\Delta_d S^o(T) . \quad (11)$$

The values of $\Delta_d H^o(T)$ and $\Delta_d S^o(T)$ depend on the change of heat capacity of dissolution $\Delta_d C_p$:

$$\Delta_d H^o(T) = \Delta_d H^o(T_o) + \int_{T_o}^T \Delta_d C_p(T'') dT'' \quad (12)$$

and

$$\Delta_d S^o(T) = \Delta_d S^o(T_o) + \int_{T_o}^T \Delta_d C_p(T'') dT''/T'' \quad (13)$$

$T_o = 298.15$ K is taken as the reference temperature. Assuming the constant value of the heat capacity change $\Delta_d C_p$ (neglecting its temperature dependence), integration of Eqs (2) and (3) yields:

$$\Delta_d H^o(T) = \Delta_d H^o(T_o) + \Delta_d C_p(T - T_o) \quad (14)$$

and

$$\Delta_d S^o(T) = \Delta_d S^o(T_o) + \Delta_d C_p \ln (T/T_o) \quad (15)$$

RESULTS

Solubility boundaries for Mg, Ca, Sr and Ba laurates at 20 °C are presented in Figure 1. Deviation of experimental points from the straight lines of slope $-1/2$ is noticeable at higher ionic strengths, where activity coefficients are significantly lower than 1. Values of K_s^o at 20 °C were calculated using experimental points at moderate and low ionic strengths because in this region Eq. (5) well describes the system. The results are in agreement with the literature data.²⁰ At higher temperatures, the experiments

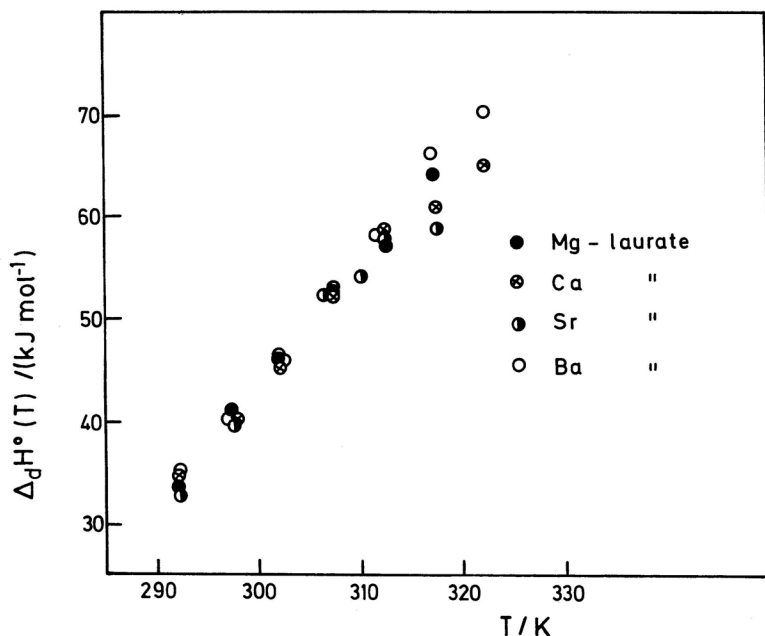


Figure 3. Enthalpies of dissolution of alkaline earth laurates *vs.* temperature. The values of $\Delta_d C_p$ calculated from the slopes of straight lines are given in Table II. The reference temperature was taken as $T_0 = 298.15$ K.

were performed in the equivalence region only and are presented in terms of equilibrium constants in Figure 2. The linear dependence of $\ln K_s$ on temperature was obtained for all salts except for Ca-laurate. Dissolution enthalpies $\Delta_d H^\circ$, calculated from the slopes of straight lines, yielded the value of approximately 52 kJ mol^{-1} for all alkaline earth laurates. In Figure 3, reaction enthalpies $\Delta_d H^\circ$ (as measured by calorimetry) are plotted as a function of the temperature for different laurates. Linear increase of $\Delta_d H^\circ$ with temperature is due to positive and constant $\Delta_d C_p$. The slopes according to Eq. (14) are equal to $\Delta_d C_p$, being approximately $1.1 \text{ kJ mol}^{-1} \text{ K}^{-1}$ for all salts.

The values of $\Delta_d S^\circ$ were calculated from solubility and calorimetric data using Eq. (11) and are plotted as a function of $\ln(T/K)$ in Figure 4. The mean value of these slopes gave $\Delta_d C_p$ of $1.1 \text{ kJ mol}^{-1} \text{ K}^{-1}$ (Eq. 15), which is in agreement with calorimetric results.

TABLE I
The interplanar distances of calcium laurate (CaL)

$T/^\circ\text{C}$	CaL ₂ (susp.)	CaL ₂ (dried)
	$D/\text{\AA}$	
20	34.7 ± 0.1	34.5 ± 0.1
50	33.4 ± 0.2	34.5 ± 0.1

TABLE II

Thermodynamic parameters for dissolution of alkaline earth laurates, calculated from calorimetric and solubility data

	Mg	Ca	Sr	Ba
$\Delta_d C_p / \text{kJ mol}^{-1} \text{K}^{-1}$ (from $\Delta_d H^\circ$)	1.19	1.14	1.09	1.09
$\Delta_d C_p / \text{kJ mol}^{-1} \text{K}^{-1}$ (from $\Delta_d S^\circ$)	1.19	1.09	1.10	1.10
$\Delta_d H^\circ(298 \text{ K}) / \text{kJ mol}^{-1}$	40.5	40.7	39.8	40.2
$\Delta_d S^\circ(298 \text{ K}) / \text{J mol}^{-1} \text{K}^{-1}$	-66.5	-97.9	-76.6	-84.8
$\Delta_d G^\circ(298 \text{ K}) / \text{kJ mol}^{-1}$	60.3	69.8	62.9	65.2

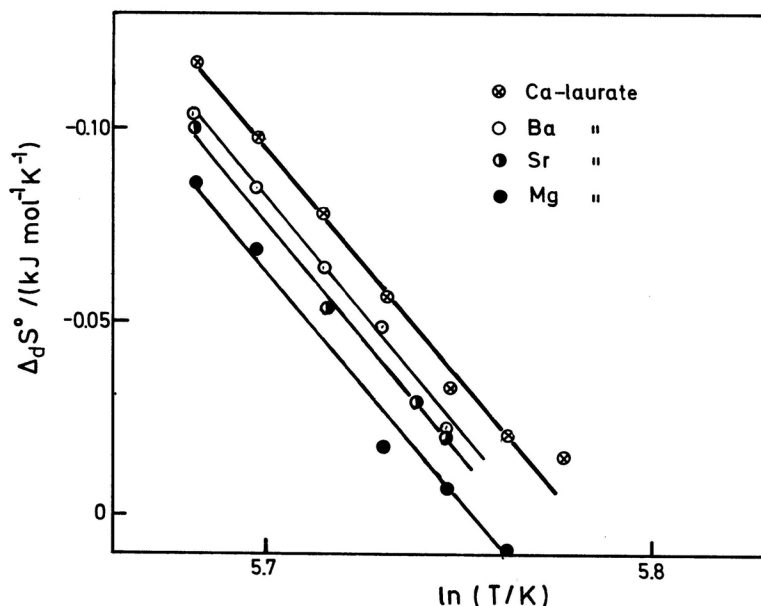


Figure 4. Standard reaction entropies of dissolution of alkaline earth laurates as a function of $\ln(T/K)$. The values of $\Delta_d C_p$ calculated from the slopes of straight lines are given in Table II.

The effect of temperature on the structure of calcium laurate was studied by X-ray diffraction. The crystal structure was analyzed in suspension and also as a dry sample. The results are presented in Table I. At higher temperature, the distances between diffraction maxima were found to be smaller for suspension. This may be explained by considering the structural changes of water molecules between layers. This effect can also be the reason for the linear entropy-enthalpy compensation effect. As expected, dried crystalline samples showed no temperature effect on the structural parameters.

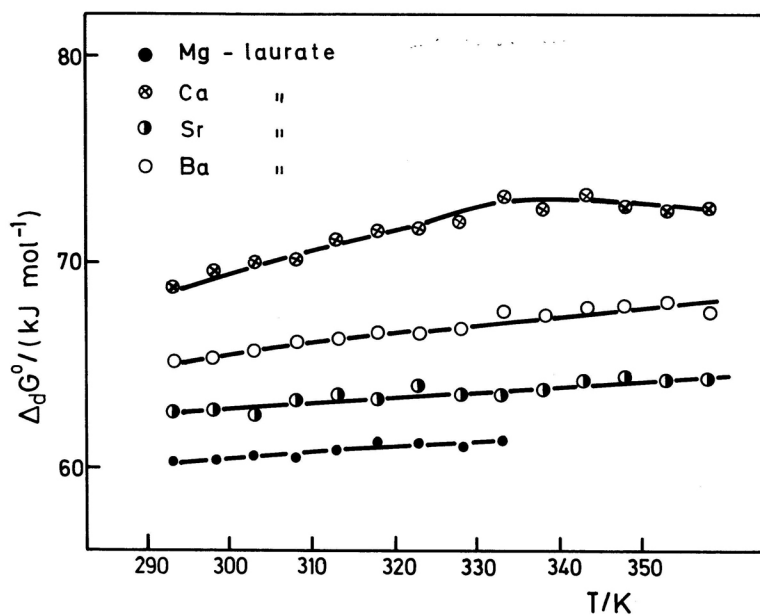


Figure 5. Gibbs energy of dissolution of alkaline earth laurates as a function of temperature.

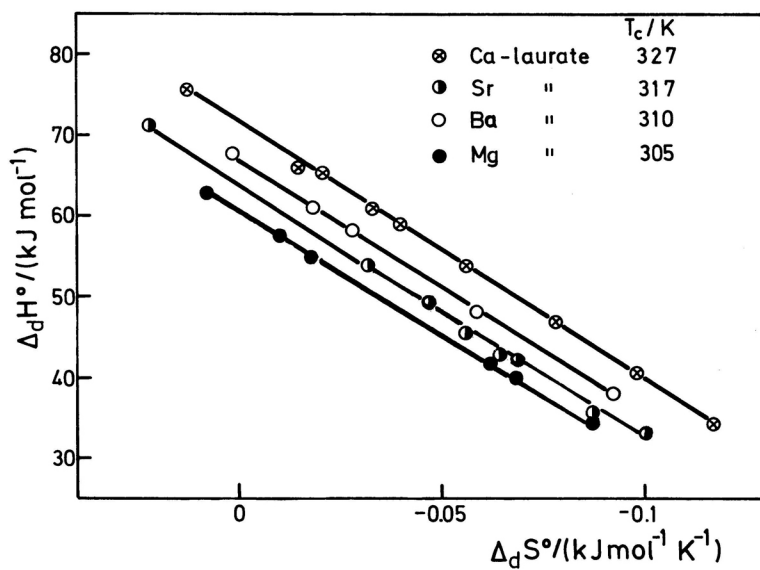


Figure 6. Enthalpy-entropy relationship for Mg, Ca, Sr and Ba-laurates. The slopes of straight lines correspond to the »critical compensation temperatures« of $T_c \approx 315 \text{ K}$.

DISCUSSION

Precipitation or dissolution of various ionic surfactants was found to be accompanied with a considerable heat capacity change.¹¹⁻¹⁴ The heat capacity change of dissolution ($\Delta_d C_p$) of silver laurate¹¹ and of barium dodecylsulfate¹² was found to be 0.7 kJ mol⁻¹ K⁻¹ and 1.4 kJ mol⁻¹ K⁻¹, respectively. The heat capacity changes of dissolution for all alkaline earth laurates, calculated from $\Delta_d H^0$ *v.s.* T and $\Delta_d S^0$ *vs.* $\ln T$ plots, are presented in Table II. The calorimetric values of $\Delta_d H^0$ and $\Delta_d S^0$ at 25 °C, calculated from equations (14) and (15), respectively, together with $\Delta_d G^0$ values at 25 °C, are also listed in the Table. All salts exhibit approximately the same $\Delta_d C_p$ and $\Delta_d H^0$ values, while $\Delta_d S^0$ and $\Delta_d G^0$ are dependent on the cation nature. The lowest solubility (highest $\Delta_d G^0$), due to the most negative $\Delta_d S^0$, was found for calcium laurate, which was not expected regarding the Ca-ion size. The same sequence of solubilities was observed for alkaline earth salts of other fatty acids (myristic, palmitic and stearic acids).²⁰ In contrast, surface active agents like dodecylbenzenesulfonate²¹ showed regularity, *i.e.* a solubility increase in the order Ba < Sr < Ca < Mg. Accordingly, the explanation for the special behaviour of calcium salts of fatty acids lies in the irregular entropy change. The effect is probably connected with hydration phenomena. The significant change in heat capacity, in the course of dissolution, results from the temperature dependency of $\Delta_d H^0$, so that simple linearization ($\ln K_s^0$ *v.s.* $1/T$) cannot be applied.¹⁴ However, owing to the scatter of experimental points, the function may appear linear and in that case the slope corresponds to the mean enthalpy change or mean temperature. The value of $\Delta_d H^0$ obtained from the solubility is approximately 52 kJ mol⁻¹, which corresponds to the temperature region from 20 to 90 °C. This value differs from the calorimetrically obtained values at 25 °C by approximately 12 kJ mol⁻¹ (Table II).

Figure 5 shows the standard Gibbs energy change as a function of temperature. Except for calcium salt, $\Delta_d G^0$ is almost independent of temperature (with respect to enthalpy dependence, Figure 3.). Such behaviour is sometimes interpreted as »compensation effect«²²; the change in enthalpy being »compensated« by an equivalent change in entropy. The linear relationship between enthalpy and entropy for all the laurates examined, with a slope of about -315 K, is presented in Figure 6. This slope, having a dimension of temperature, commonly called²² the »critical compensation temperature« T_c , could be explained on the basis of Eqs. (14,15) yielding:

$$d(\Delta_d H^0(T))/d(\Delta_d S^0(T)) = T \quad (16)$$

Accordingly, T_c is not a »critical« temperature for given reactions, but just an average temperature within the examined temperature range. For example, 315 K lies within the examined temperature region (290 to 330 K).

CONCLUSION

This work shows that alkaline earth laurates differ in $\Delta_d S^0$ but not in $\Delta_d H^0$ and $\Delta_d C_p$. The change in entropy for Ca- laurate was found to be the lowest (highest negative value), which explains the irregular solubility sequence for alkaline earth carboxylates, *i.e.* the reason for the lowest solubility of calcium salt. Analysis of the so called »compensation effect« (constant $\Delta_d G^0$; linear dependence of $\Delta_d H^0$ *vs.* $\Delta_d S^0$) has shown that »critical compensation temperature« is just an average temperature within the examined temperature range.

Acknowledgment – The authors are grateful to Prof. Vl. Simeon and to Dr. M. Tomić for fruitful discussion and for their constructive criticism of the manuscript. We wish to express our gratitude to dr. S. Popović for the X-ray analysis of crystalline phases.

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SAŽETAK

Termokemija taloženja zemnoalkalijskih laurata

Vesna Hrust i Đurđica Težak

Istraživana je temperaturna ovisnost topljivosti zemnoalkalijskih laurata u vodenim otopinama. Entalpije otapanja soli određene su kalorimetrijski pri raznim temperaturama i uspo-ređene s podacima dobivenima iz topljivosti. Entalpija otapanja $\Delta_d H^\circ$ pokazuje linearnu ovisnost o temperaturi. Promjena reakcijskoga toplinskog kapaciteta $\Delta_d C^\circ$, izračunana iz ovisnosti $\Delta_d H^\circ$ u. T iznosi 1.1 kJ mol^{-1} za sve soli.

Na temelju kalorimetrijskih mjerenja i mjerenja topljivosti određena je entropija otapanja $\Delta_d S^\circ$, koja je linearna funkcija $\ln T$; $\Delta_d C_p$ izračunan iz ovih prikaza jednak je vrijednosti dobivenoj iz temperaturne ovisnosti entalpije.

Ponašanje svakoga zemnoalkalijskog kationa očituje se u promjeni entropije otapanja $\Delta_d S^\circ$. Entropija otapanja najniža je za kalcijevu sol što objašnjava njezinu neregularno nisku topljivost.

Takozvani kompenzacijski efekt tumači se pomoću »kritične kompenzacijske temperature«, za koju je nađeno da ima značenje srednje vrijednosti temperatura unutar ispitivanog područja.