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DIFFERENTIAL THERMAL ANALYSIS OF *n*-LONG CHAIN ALCOHOLS AND CORRESPONDING ALKOXY ETHANOLS*

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ABSTRACT

The differential thermal analyses of *n*-long chain alcohols $CH_3(CH_2)_{n-1}$–OH, designated as C_n–OH (n = 16, 18, 20 and 22), and corresponding alkoxy ethanols $CH_3(CH_2)_{n-1}$–OCH_2CH_2OH, designated as C_n–OC_2H_4OH, have been carried out at a heating rate of 1 °C min^{-1}. The differential e.m.f. (ΔV) has been plotted against the temperature of the reference material (°C) and the onset of the peak has been taken as the appearance of the polymorphic phase transition or melting of the compound. Heats of transition (ΔH_t) and melting or fusion (ΔH_f) were computed from the areas under the respective peaks.

INTRODUCTION

It has been well known for over 40 years that insoluble monomolecular films of *n*-long chain alcohols retard the evaporation of the underlying water to a significant extent. In recent years, considerable interest has developed in the practical utilization of this effect towards water conservation from lakes and reservoirs. It was found that especially cetyl alcohol (C_{16}–OH) by itself or when mixed with stearyl alcohol (C_{18}–OH) was perhaps the best among the substances so far studied in the laboratory, though in the field these films often give poor results. Preliminary investigations[1, 2] showed that the alkoxy ethanols, obtained by condensing one ethylene oxide molecule with the alcohols, were rather promising and gave better evaporation reduction than the alcohols used.

With a view to illucidating the behaviour of these compounds in the monolayer state, it is necessary to investigate the temperature dependence of the bulk phase modifications exhibited by the above compounds. Differential thermal analysis (DTA) provides information regarding transition temperatures and the number of phase modifications. The associated thermodynamic quantities are likely to provide

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valuable information in determining the thermal stability as related to crystal structure and lattice energy of the crystalline state.

From the literature survey, it appears that very little systematic work has been done along these lines. Most of these studies were confined to the alcohols only. Earlier, Mumford and Phillips[3], Smith[4], Bernal[5], Meyer and Reid[6] and others determined the polymorphic modifications in the alcohols by thermal analysis. Kolp and Lutton[7] observed the polymorphism in fatty alcohols, C_{16}–OH and C_{18}–OH, by X-ray diffraction and thermal methods. The α-form (hydrocarbon chain is vertical to the plane of the end group and rotating) appears in the melt and freezing point, and exists as a metastable form in a narrow temperature range near the melting point, which gradually transforms to the stable γ-form. In the γ-form, the hydrocarbon chain is inclined to the plane of the end group and non-rotating. The abrupt cooling of the α-form causes transformation to the β-form (hydrocarbon chain is vertical to the plane of the end group and non-rotating) which also gradually changes to the γ-form on ageing. Vines and Meakins[8] investigated the phase transformations in two different kinds of commercial cetyl alcohol pellets, one containing less stearyl alcohol and the other being of high content, by dilatometric measurements (heating and cooling curves), X-ray and dielectric studies. Watanabe[9] observed polymorphism of even-carbon-membered alcohols from C_{12} to C_{34} by X-ray and thermal arrest methods. He observed that the transitions from C_{14} to C_{26} are reversible, whereas transitions from C_{28} to C_{34} are irreversible, appearing only on cooling.

In the present work, the results on the differential e.m.f. measurement of four *n*-fatty alcohols, $CH_3\ (CH_2)_{n-1}$–OH, designated as C_n–OH (n = 16, 18, 20 and 22) and corresponding alkoxy ethanols $CH_3\ (CH_2)_{n-1}$–OCH_2CH_2OH, designated as C_n–OC_2H_4 OH, as a function of temperature, are reported.

EXPERIMENTAL

The DTA apparatus used in the experiments consisted of two identical cylindrical stainless steel cells, containing sample and reference material (Nuzol), respectively placed coaxially in an electrically heated, adequately thermally insulated cylindrical furnace as described by Vold[10]. Cell dimensions were 4.0 cm long with an internal diameter of 1.25 cm. The heating runs were followed at a constant heating rate of about 1 °C min^{-1}. The differential temperature and the temperature of the reference material were measured with a Cu–constantan thermocouple (30 s.w.g.) located at the centres of the two cells and the readings were noted every 30 ± 1 sec.

As usual, temperatures of the reference (°C) were plotted against differential e.m.f. (μV). Occurrence of the peaks was noted as phase transitions and the heats of transitions were computed from the areas under the peaks. Since the temperatures of the reference cell were noted, the initiations of the peaks were recorded as the transition temperatures.

The heat evolved, ΔH, is equal to

$$\Delta H = \psi \int_{t}^{t_r} Q\mathrm{d}t$$

where ψ is the proportionality constant and was evaluated experimentally by calibrating the apparatus with the known heat of fusion of stearic acid[10] (47.6 cal g^{-1}).

All the alcohols and alkoxy ethanols used were fractionally distilled and recrystallised several times to obtain 99.9% pure compounds. The purity of each was checked in a gas chromatograph (Aerograph). However, C_{20}– and C_{22}–OC_2H_4OH were found to be only 98% pure.

At least three repeated experiments were run for each sample and the reproducibility of the transition temperatures and heats of transition was within ±0.25 °C and ±0.2 kcal $mole^{-1}$, respectively.

RESULTS AND DISCUSSION

Alcohols

In Fig. 1, the DTA runs of C_{16}–, C_{18}–, C_{20}– and C_{22}– alcohols have been plotted taking the x-axis as the temperature of the reference (Nujol) in °C and the y-axis as the differential e.m.f. in microvolts (μV). It can be seen that C_{16}–OH, C_{20}–OH and C_{22}–OH each exhibited two distinct peaks, one just before the fusion temperature and the other corresponding to fusion. In the case of C_{18}–OH, the appearance of a hump prior to the fusion peak is indicative of a solid state transition,

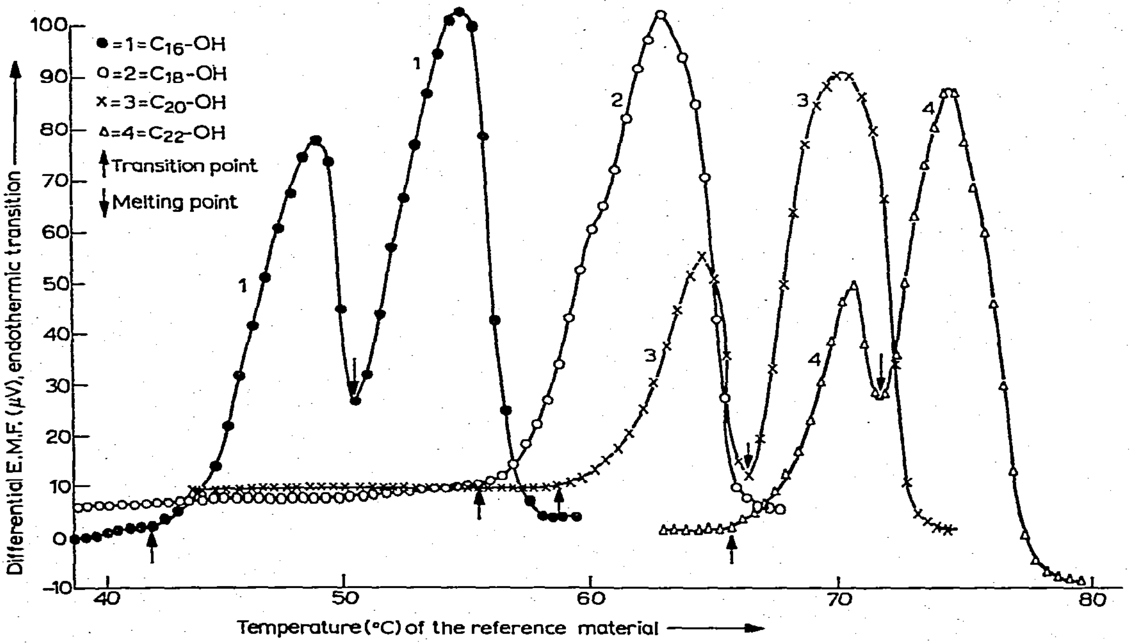

Fig. 1. Differential thermal analysis graphs for n-long chain alcohols (C_n–OH, n = 16, 18, 20 and 22). Heating rate = 1 °C min^{-1}.

TABLE 1

DTA DATA OF *n*-LONG CHAIN ALCOHOLS AND ALKOXY ETHANOLS

Compound	*M.p. of the cryst-alline subs-tance (°C)*	*Solid state transition temp. (°C)*		*Fusion temp. (°C)*		ΔH_t *(kcal mole⁻¹)*	ΔH_f *(kcal mole⁻¹)*	$\Delta H_F = \Delta H_t + \Delta H_f$ *(kcal mole⁻¹)*		ΔS_t *(cal mole⁻¹ deg⁻¹)*	ΔS_f *(cal mole⁻¹ deg⁻¹)*	$\Delta S_F = \Delta S_t + \Delta S_f$ *(cal mole⁻¹ deg⁻¹)*		*Lit. value of transition temp. (°C)*
		Onset	*Max.*	*Onset*	*Max.*			*Present value*	*Lit. value*			*Present value*	*Ref. 13*	
C_{16}-OH	49.7	41.9	48.9	50.5	54.8	5.07	8.12	13.19	13.6[c] 13.8[d] 12.4[e]	16.1	25.1	41.2	43.0 ± 3.1	45.7[a] 48.4[b]
C_{18}-OH	58.5	55.3			62.9	4.50	9.36	13.86	17.7 ± 1.6[d]	13.7	28.1	41.8	53.7 ± 2.1	54.5[a] 55.0[b]
C_{20}-OH	64.9	58.8	64.5	66.4	70.4	3.33	10.00	13.83	23.7 ± 1.6[d]	11.5	29.5	41.0	70.1 ± 3.1	63.5[a] 62.0[b]
C_{22}-OH	70.3	66.7	70.8	72.0	74.9	4.12	11.13	15.25	21.8 ± 2.8[d]	12.1	32.3	44.4	63.7 ± 8.4	67.6[a] 68.0[b]
C_{16}-OC_2H_4OH	42.7	35.0	42.0	43.5	47.0	3.57	8.92	12.49		11.6	28.2	39.8		41.4[b]
C_{18}-OC_2H_4OH	51.2	41.0	47.4	50.3	55.7	3.77	9.12	12.89		12.0	28.2	40.2		40.4[b]
C_{20}-OC_2H_4OH	59.8	39.5	45.3	58.6	62.9	3.48	10.43	13.91		11.1	31.5	42.6		39.0[b]
C_{22}-OC_2H_4OH	64.4	44.0	50.3	62.7	67.7	3.09	10.50	13.59		9.7	31.3	41.0		45.0[b]

[a] Ref. 9; [b] ref. 12; [c] ref. 15; [d] ref. 13; [e] ref. 14.

but it could not be resolved by keeping the rate of heating at 1 °C min^{-1}. It is obvious from the graph that there is a gradual shift of transition and fusion peaks to a higher temperature with increase in chain length. The values of transition and fusion temperatures are given in Table 1 to illustrate this increase. In the case of C_{18}–OH, since the peaks for the phase transition in the solid state and fusion were overlapping, the initiation of the fusion peak could not be distinguished. The values of transition temperatures of *n*-long chain alcohols reported by Watanabe[9] from thermal analysis and X-ray methods have been given in Table 1 for comparison. In the case of C_{16}–OH and C_{22}–OH, our values appear to be a little lower. The three forms of hexadecanol could not be revealed, although Watanabe et al.[11] indicated that this compound is trimorphic in the solid state, and on heating the low temperature β- and γ-forms transform to the high-temperature α-form. Watanabe[9] reported the transition point of C_{16}–OH at 45.7 °C, while we observed it at 41.9 °C. Presumably, the transition peak noted in our studies is for $\beta \rightarrow \alpha$ as well as $\gamma \rightarrow \alpha$, since both β- and γ-forms will be present in equilibrium with one another at a particular temperature. Moreover, the transition phenomenon has been known to be affected by the variations in the measurement techniques and thermal histories of the material. The values of transition and fusion temperatures obtained by dielectric measurements by Pradhan et al.[12] for the same grade of compounds are in good agreement with our values (Table 1).

The heat of transition, ΔH_t, showed a decreasing trend with the increase in chain length (Table 1), which varies from 316 cal mole^{-1} per CH_2 group for C_{16}–OH to 187 cal mole^{-1} per CH_2 for C_{22}–OH. Davies and Kbett[13] reported 298 cal mole^{-1} per CH_2 for C_{16}–OH in the phase transition from γ to α. The subsequent decrease with chain length in the contributions per CH_2 can be attributed to the tilts of the CH_2 chain axis to the surface normal as the chain lengthens. From the X-ray diffraction studies of *n*-alcohols, the estimated tilts for C_{16}–OH through C_{22}–OH fall from 33 to 31°, respectively. The corresponding tilts in the α-form for C_{16}– through C_{22}–OH are 6 and 16°, respectively. From the values of the above tilts, it may be seen that $\gamma \rightarrow \alpha$ transformation the alkyl chain has to move through lesser angles with increase in chain length, being about 27° for C_{16}–OH and 15° for C_{22}–OH. This explains the decrease in contribution per CH_2 group to ΔH_t with the increase in chain length.

The heat of fusion, ΔH_f, increases as the chain length increases from C_{16} to C_{22}. Comparison of the magnitudes of heat of transition and heat of fusion for a particular compound showed that almost 2/3 to 1/3 of the thermal energy has already being consumed for the phase transition prior to melting. If it is assumed that the real heat of fusion (ΔH_F), i.e. the heat required to obtain the fused material for the melting of these compounds, is the sum of ΔH_t and ΔH_f, then, for C_{16}–OH, the observed ΔH_F value (13.2 kcal mole^{-1}) is in good agreement with the values reported by Parks and Rowe[14] (12.4 kcal mole^{-1}) measured from heats of solution, and Kakiuchi et al.[15] from specific heat measurements (13.6 kcal mole^{-1}). Timmermans[16] estimated it cryscopically as 8.3 kcal mole^{-1}; these data probably need to be corrected for a phase change energy from the $\gamma \rightarrow \beta$ form. Davies and Kbett[13] estimated the values of ΔS_F and ΔH_F, given in Table 1 for comparison, from the difference in the corresponding values for sublimation and vaporisation at the fusion temperature for C_{16}– to C_{22}–OH. It appears that except for C_{16}–OH, the reported values are a little higher than those obtained by us. They mentioned that the estimated values for the fusion process are more uncertain than the individual factor from which they are derived. The increasing trend of ΔH_F and ΔS_F with the increase in chain length is in agreement with the above authors.

A linear relationship has been found by plotting ΔH_F against n (number of C atoms) as observed in other homologous series. The equation for n-alcohols is

$$\Delta H_F = 7.7 + 0.34n \tag{1}$$

A meaningful analysis of the data can be offered in terms of "group contributions". Such group contributions will vary slightly from one homologous series to another, i.e. they are dependent on nearest neighbour interactions and the precise group environment (e.g. for the CH_2 group), is not reproduced in different series. Equation (1) provides a value of 0.34 kcal mole^{-1} as the contribution per CH_2 group to the lattice energy. The constant term, 7.7 kcal mole^{-1}, represents the composite contribution of terminal –CH_3CH_2 and –OH groups. The contribution due to the terminal CH_3CH_2 groups is 0.8 kcal mole^{-1}. Hence, the contribution due to total hydroxyl group comes out to be 6.9 kcal mole^{-1}. This value is a little less than 8.0 kcal mole^{-1} as suggested to be the total hydroxyl group interaction energy in the crystalline n-alcohols as reported by Davies and Kbett[13]. Mathews and Sheets[17] have reported an average hydrogen bond energy at 300 K as 6.8 ± 0.2 kcal mole^{-1} in carboxylic acid dimers determined from vapour density, IR and absorption measurements. In evaluating the hydrogen bond energy in OH · · · OH groups they have given the most probable value for the unassociated OH group as 2.0 ± 0.4 kcal mole^{-1}. Assuming this value, the OH · · · OH hydrogen bond energy in the crystalline alcohols has been reported as equal to 6.0 kcal mole^{-1} with an uncertainty ±10%, while we obtained a value of 4.9 kcal mole^{-1}.

In the case of C_{20}–OH, the ΔH_F appears to be lower than its expected sequence with its other homologues. Davies and Kbett[13] reported a similar anomaly in their sublimation data and assigned this as being due to its abnormal behaviour in the vapour phase. However, we presume that even in the liquid phase C_{20}–OH exhibited anomalous behaviour. The results of surface tension measurements[18] in the liquid state also indicate the abnormality for C_{20}–OH.

With increase in chain length, ΔS_F shows an increasing trend. The X-ray studies made by Watanabe[9] suggest that, in the α-form, the inclination of the chains to the plane of the end group increases as the chain lengthens. The opacity of the α-form also increases and the side spacing splits into two lines. These observations indicate that with the increase in the chain length, the deviation in configuration or molecular motions from the typical rotational state may increase. It was also suggested that, instead of molecular rotation, molecular vibrations around the axis may also take place in such long-chain compounds, which may cause an increase in entropy with chain length.

From the X-ray, dielectric and IR analysis of *n*-long chain alcohols it is established that in the α-form, the molecules are loosely packed compared with the γ-form. This explains the increase in entropy observed after the transition has occurred. It is believed, judging from the X-ray data, that the crystal in the α-form is of the hexagonal type. On melting, the long range forces are destroyed and the molecules change from hexagonal array to more or less rectangular array with increased freedom of rotations and oscillations which explains the increase in entropy on melting of these alcohols. The IR studies of these compounds revealed that the γ-form is composed of *trans* and *gauche* molecules, while in the α-form or in liquid state, *gauche* molecules predominate. This explains the contribution of the end group to the increase of entropy, when the phase transformation γ to α and melting occurs.

Alkoxy ethanols

In Fig. 2, typical curves of temperature of the reference material (°C) vs. differential e.m.f. have been shown for C_{16}–, C_{18}-, C_{20}-, C_{22}–OC_2H_4OH. It can be seen that all the alkoxy ethanols distinctly exhibited two peaks, one for the crystalline phase transformation prior to fusion and the other for the fusion of the material. It is obvious from the graph that there is a gradual shift of transition and fusion peaks to higher temperature with the increase in the chain length. The values of the transition and fusion temperatures are given in Table 1.

The lower transition temperature value shown by C_{20}–OC_2H_4OH may be

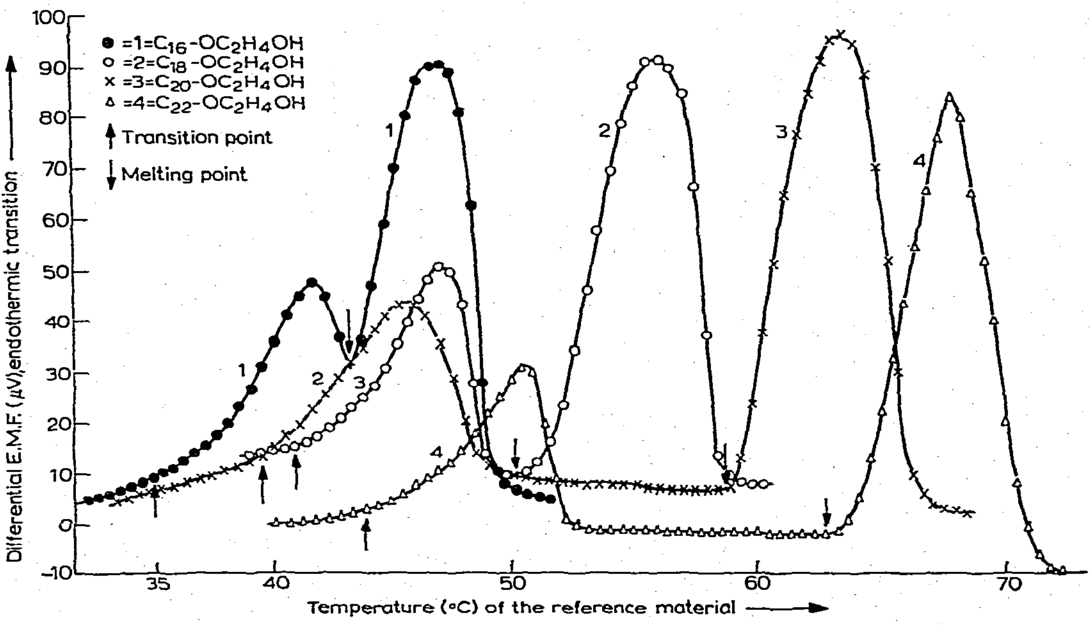

Fig. 2. Differential thermal analysis graphs for *n*-long chain alkoxy ethanols (C_n–OC_2 H_4OH, $n = 16$, 18, 20 and 22). Heating rate = 1 °C min^{-1}.

attributed to 2% impurity present. The values of transition temperatures are in good agreement with those of the dielectric values obtained by Pradhan et al.[12] (Table 1).

From the curves it is noteworthy that as the chain length increases the separation of the transition and fusion peaks also increases, being least for C_{16}–OC_2H_4OH and maximum for C_{22}–OC_2H_4OH.

From Table 1, it is clear that the heat of transition decreases as the chain elongates in the case of alkoxy ethanols. It can be well visualised from X-ray diffraction studies that the tilts of the alkyl chain axis to the surface normal vary from about 14 to 17° in the γ-phase and 8 to 16° in the α-phase for C_{16}–OC_2H_4OH to C_{22}–OC_2H_4OH, respectively. For the solid phase transformation from γ to α form, the alkyl chain travels through lesser angles as the chain increases. For a particular compound the value of the heat of fusion is about 2.5 to 3.0 times higher than that of the heat of transition. It means that, prior to fusion, a solid phase transformation has occurred which requires about 1/3 of the thermal energy needed for fusion. It can also be observed that, with the increase in the chain length, ΔH_t decreases while aggregate $\Delta H_F(\Delta H_t + \Delta H_f)$ increases. The ΔH_F was found to be linear between C_{16} and C_{22} except that C_{20} exhibits a little higher value.

The above linearity can be represented by

$$\Delta H_F = 9.6 + 0.18\,n \tag{2}$$

The constant term 9.6 kcal mole^{-1} is the composite contribution of the end groups, whereas the 0.18 kcal mole^{-1} is the contribution per CH_2 group to the lattice energy.

The ΔS_F cal mole^{-1} deg^{-1} indicates an increasing trend as the chain length increases. For a particular compound ΔS_f is roughly three times ΔS_t, indicating that in fusion about three times more disorder and freedom of movement are experienced by the molecules as compared to that in the solid phase modification.

It is believed from the IR studies that, in the melt, the $-OCH_2CH_2OH$ group exhibits predominantly *gauche* configuration, while in the solid, both *gauche* and *trans* configurations are present in nearly equal numbers.

X-ray analysis revealed that the alkoxy ethanols exhibit γ-phase modification at room temperature. On heating the material, γ-phase transforms to α-phase. From the short spacings, the molecular packing in the α-form was found to be loose compared with that in the γ-phase. In polymorphic transformation γ to α, that is, for bringing the tilted molecules to nearly perpendicular positions and converting the *trans* to *gauche* configuration, the thermal energy has to be supplied from outside, affecting the corresponding increase in entropy.

On melting from the hexagonal form, the structure becomes more or less orthorhombic and the intermolecular binding appreciably diminishes compared with that in the solid state. Correspondingly, an increase in volume also occurs due to the creation of holes. This entails an increase in entropy of the system due to available freedom of movement of the molecules.

Comparison of n-alcohols and corresponding alkoxy ethanols

Our main interest is to understand the difference in structural aspects of alcohols and alkoxy ethanols which are likely to provide valuable information about the superiority of the latter, when both are being used for reducing the water evaporation by spreading them as insoluble monolayers.

By comparing Figs. 1 and 2, it may be seen that the DTA curves observed for the compounds of both series are similar in nature. Two distinctly resolved peaks are exhibited in each series except C_{18}–OH, one for the solid phase transformation (γ to α) prior to fusion and the other for the fusion of the compound. The separation of the transition and fusion points is remarkably more in the case of alkoxy ethanols than in alcohols, while the transition peaks ascend more steeply in the case of alcohols than alkoxy ethanols, indicating gradual transformation in the latter case.

In both the series of compounds, both transition and fusion temperatures are shifted to a higher temperature with increase in chain length. With the extension of the polar group by $-OCH_2\ CH_2$, the fusion temperature decreases by about 6–7 °C, keeping the C-chain constant, while the difference between the transition temperatures of alcohols and corresponding alkoxy ethanols goes on increasing as the chain length increases.

The fusion temperatures of alcohols by the DTA technique is higher (~1 °C) than was observed by the capillary method; while in alkoxy ethanols, the reverse is observed, probably due to the supercooling tendency of the alkoxy ethanols. A similar trend has also been observed in dielectric studies[12].

For both the series of compounds, heat of transition decreases whereas heat of fusion increases with increase in chain length. The numerical values of ΔH_t and ΔH_f are less in the case of alkoxy ethanols than the corresponding alcohols. This indicates that the intermolecular attraction is also less in the former case due to the greater dipole–dipole repulsion effect, which is evident from their lower melting points.

As mentioned above

$$\Delta H_F = 7.7 + 0.34n$$

for alcohols and

$$\Delta H_F = 9.6 + 0.18n$$

for alkoxy ethanols.

The energy contribution due to the end groups in the case of alkoxy ethanols (9.6 kcal mole^{-1}) is more than that of the alcohols (7.7 kcal mole^{-1}), indicating the stronger interaction of the end groups in the former case. The energy contribution per CH_2 group to the lattice energy in alcohols (0.34 kcal mole^{-1}) is more than alkoxy ethanols (0.18 kcal mole^{-1}), indicating looser packing in the latter case. This is in agreement with X-ray data.

The aggregate value of ΔS_t and ΔS_f increases as the chain length increases in both the series. The ΔS_f is nearly 2–3 times higher than ΔS_t, showing that nearly 2–3 times greater disorder is taking place in melting than transition.

In the case of C_{16}–OH, Stewart[19] and others reported that crystals in the β-form spread faster in comparison to those in the α-form. Moreover, on the water surface the γ-form converts into the β-form and hence the spreading rate for the γ-form remained obscure. The observed higher rate of spreading in *n*-alkoxy ethanols compared with *n*-alcohols can be visualised from the thermodynamic and structural studies. The values of the heat of transition for *n*-alkoxy ethanols are lower than the corresponding *n*-alcohols, indicating the easier phase transition into the α-form from the γ-form. The transition points in the former case are lower, approaching room temperature, and they decrease further in the presence of water. The rate of spreading from the bulk into a monolayer on the water surface is higher when the temperature increases. From the above considerations, it can be analysed that the faster spreading β-phase modification is thermodynamically facilitated at lower temperatures in alkoxy ethanols than in alcohols due to which alkoxy ethanols exhibit higher rates of spreading. In addition, *n*-alkoxy ethanols possess two oxygen atoms which are strong proton-acceptors, increasing the effective attraction for the OH group in the water substrate influencing the inter- and intrahydrogen bonding in the monolayer state.

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