Differential Thermal Analysis of Mixtures of Long Chain Primary Alcohols & Alkoxy Ethanols†

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The differential thermal analysis of the mixtures of some long chain primary alcohols and alkoxy ethanols, viz., C_{16}—OH + C_{22}—OH; C_{16}—OC_2H_4OH + C_{22}—OH and C_{16}—OH + C_{22}—OC_2H_4OH in various molar proportions (1:99; 5:95; 50:50; 95:5; 99:1) has been carried out using a heating rate of 1°C/min. The onset of the DTA peak is taken as the appearance of the polymorphic phase transition or melting of the mixture. Heats of transition ($\triangle H_t$) and melting or fusion ($\triangle H_f$) have been computed from the areas under the respective peaks. Data have been discussed in terms of chain and polar groups interactions. Mixtures appear to form homogenous solid solutions.

IN a recent communication[1], we reported the differential thermal analysis (DTA) of some long chain primary alcohols, C_n-OH(n=16, 18, 20 and 22) and the corresponding alkoxy ethanols, C_n-OC_2H_4OH. This study provided valuable information regarding variation in polymorphic transition and fusion points with respect to the increase in chain length and polar end-group. The associated thermodynamic quantities, namely heats of transition, fusion and entropy change, were found to be structural-sensitive, depending upon the chain length and the polar group. Lower values for alkoxy ethanols as compared to those for the corresponding alcohols were attributed to loose molecular packing due to dipole-dipole repulsive interactions.

From the view point of retardation of water evaporation, alkoxy ethanols mono-layer films[2] have proved to be more efficient than alcohols. However, various mixtures of alcohols and alkoxy ethanols exhibited better performance than the individual components[3]. Therefore, it was thought worthwhile to investigate the effect of addition of higher chain compounds to lower chain compounds with —OH and —OC_2H_4OH polar end-groups, in particular, to study their homogeniety, changes in orientation and packing characterisatics beside studying the chain-chain, chain-polar and polar-polar interactions. The thermodynamic properties of such systems may be useful in elucidating the nature of packing vis-a-vis the variation in chain length as well as the nature of end-group.

In the present work, the results on the DTA measurements of the three mixtures; (i) C_{16}—OH+ C_{22}—OH; (ii) C_{16}—OC_2H_4OH + C_{22}—OH and (iii) C_{16}—OH + C_{22}—OC_2H_4OH in the molar ratios 99:1; 95:5; 50:50; 5:95 and 1:99 are reported.

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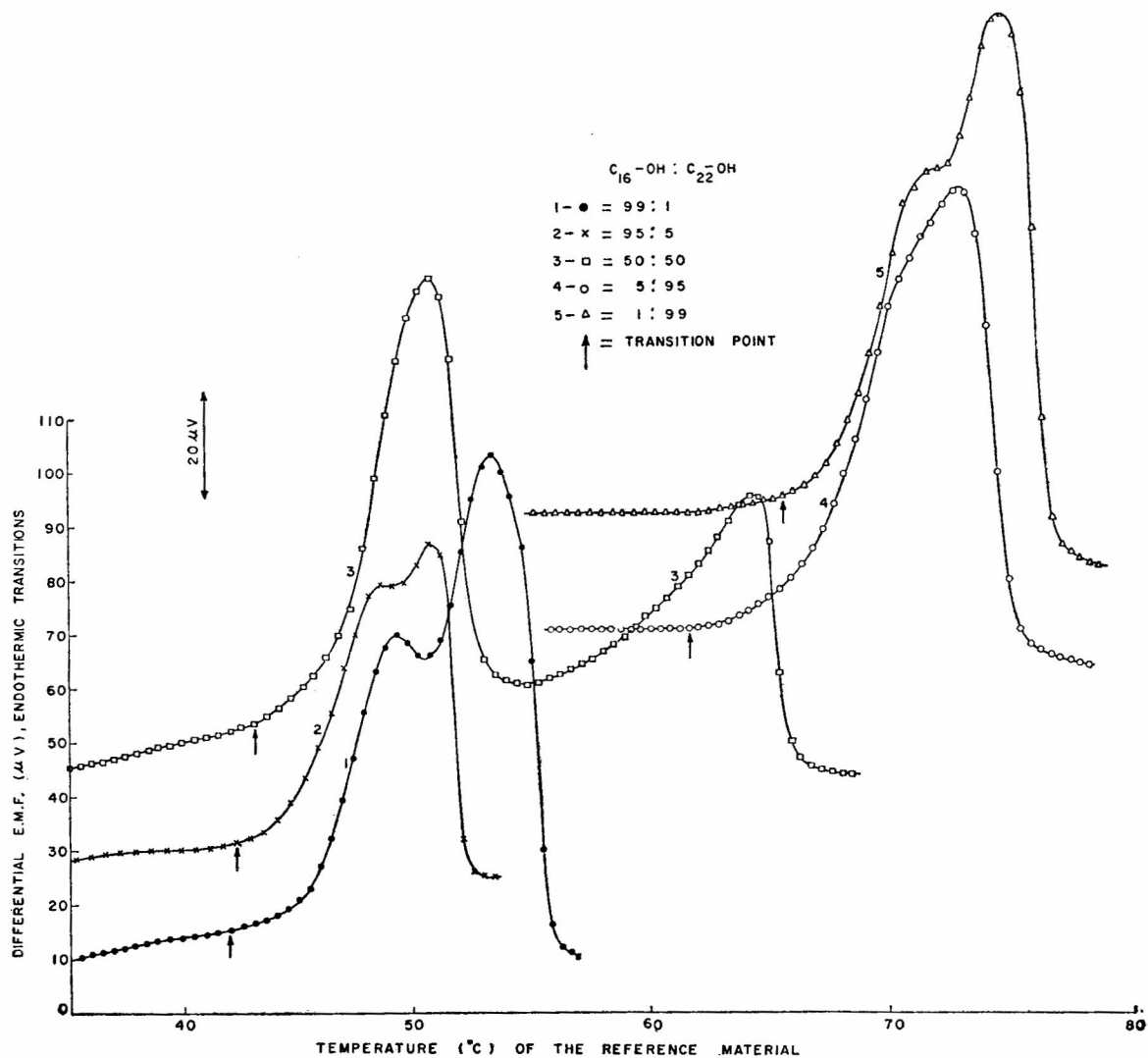‡Present address : Indian Institute of Petroleum, Dehradun.

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Materials and Methods

The apparatus and method used for measuring differential e.m.f. were the same as mentioned in the earlier communication[1]. As usual, temperatures of the reference (°C) were plotted against differential e.m.f. (μV). Occurrence of the peaks were recorded as the transitions temperatures (temperature of the reference cell). The heats of transitions were computed from the areas under the peaks. The heat evolved, $\triangle H$, is given by the equation,

$$\triangle H = \psi \int_t^{tr} \theta \cdot dt$$

where ψ is the proportionality constant. It was evaluated experimentally, by calibrating the apparatus with stearic acid whose heat of fusion is known[4] (47.6 cal/g).

All the alcohols and alkoxy ethanols used in mixtures were 99.9% pure compounds and their purity was checked by gas chromatography. However, C_{22}—OC_2H_4OH was found to be only 98.0% pure.

At least three repeated experiments were run for each sample and the reproducibility of transition temperature and heat of transition was within ±0.25°C and ± 0.2 k cal/mol respectively.

Results and Discussion

C_{16} — OH + C_{22} —OH — The DTA runs of C_{16}—OH and C_{22}—OH mixtures for different ratios are shown in Fig. 1. It may be noted that except for the 50:50 mixture (curve 3) all the other mixtures do not exhibit appreciably resolved peaks for the transition and fusion transformations, specially the 5:95 mixture (curve 4). The transition temperature goes on increasing as the percentage of C_{22} —OH in the mixture is increased (Fig. 1 and Table 1). However, the fusion temperature decreases upto 5%

Fig. 1 — DTA curves for the mixture of C_{16}—OH and C_{22}—OH in various proportions, heating rate = 1°C/min.

addition and after that it increases. On the addition of 50 mole percent of the longer chain component (C_{22} —OH) to the shorter chain component (C_{16} —OH), the fusion temperature decreases by about 13°C while that of the C_{16} —OH increases by about 7°C.

On the other hand, the transition temperature (43.4°C) of the 50:50 mixture decreases by about 23°C as compared to that of the pure C_{22} —OH[1] and increases by about 2.5°C as compared to that of pure C_{16} —OH. Thus, the transition point is influenced more than the fusion point.

Due to the overlapping of the transition and fusion peaks, $\triangle H_t$ and $\triangle H_f$ of certain mixtures could not be computed without ambiguity. However, the total area under the overlapping peaks was measured for the evaluation of $\triangle H_F = (\triangle H_t + \triangle H_f)$ and the values are given in Table 1. The $\triangle H_F$ is found to decrease abruptly, as 1% and 5% of C_{22}—OH are added to C_{16} —OH, while in equimolecular proportion, the $\triangle H_F$ value lies near the value of pure C_{22} —OH. Thereafter, it nearly remains constant

approaching the value of the higher member. The results thus indicate that the lattice energy of the shorter chain compound is affected more by addition of the longer chain compound due to chain-chain interaction. However, it may be pointed out that mixtures of C_{16} —OH and C_{22} —OH appear to be miscible homogenously as the equimolecular proportion of the two different components does not show any significant peaks of its own. In two dimensional phase behaviour studies by Kuchhal et al.[6] similar results were obtained for C_{16} —OH $+C_{22}$ —OH (50:50) mixture by surface potential measurement of mono-molecular films.

C_{16} —OC_2H_4OH + C_{22} —OH — Typical DTA (endothermic) curves for the mixture of C_{16} —OC_2H_4 OH and C_{22} —OH in different molar proportions are shown in Fig. 3. The general appearance of curves is similar to those for the above mixture except for curve 3 (50:50 mixture), where the transition peak appears to be broadened to a greater extent resulting in a smaller peak for fusion. The observed transition and fusion temperatures along with the calcula-

TABLE 1 — DTA DATA OF ALCOHOLS AND ALKOXY ETHANOL MIXTURES

Compounds (mol % ratio)	Average molec. wt.	m.p. by capillary method, (°C)	Solid state transition temp. (°C) onset (max)	Fusion temp. (°C) onset (max)	$\triangle H_t$, (kcal/mol)	$\triangle H_f$, (kcal/mol)	Total $\triangle H_t$ (kcal/mol)
1	2	3	4	5	6	7	8
C_{16}—OH (100)	242.43	49.7 49.6*	41.9 (48.9)	50.5 (54.8)	5.07	8.12	13.19
C_{16}-OH; C_{22}-OH (99 : 1)	243.28	49.1 48.7*	41.8 (48.8)	50.3 (53.3)	4.05	7.50	11.55
C_{16}-OH; C_{22}-OH (95 : 5)	246.64	48.5 47·5*	42.4 42.3**	50.0 (50.9)**	—	—	4.80
C_{16}-OH; C_{22}-OH (50 : 50)	284.51	59.5±1.0 53.5*	43.2 (50.7) 43.2** (48.5)**	55.2 (64.2) 57.0** (62.8)**	7.80	7.50	15.30
C_{16}-OH; C_{22}-OH (5 : 95)	322.37	68.4 67.7*	61.6 61.4**	(72.7) (69.8)**	—	—	14.50
C_{16}-OH; C_{22}-OH (1 : 99)	325.73	70.2 69.8*	65.6 64.3** (69.8)**	— (74.2) 70.4** (72.5)**	—	—	15.20
C_{22}-OH (100)	326.58	70.3 70.2*	66.7 (70.8)	72.0 (74.9)	4.12	11.13	15.25
C_{16}-OC$_2$H$_4$OH (100)	286.48	42.6 42.6*	35.0 (42.0)	43.5 (47·0)	3.57	8.92	12.49
C_{16}-OC$_2$H$_4$OH; C_{22}-OH (99 : 1)	286.88	42.3 42.0*	32.9 (41.1)	43.0 (47.0)	3.66	7.88	11.54
C_{16}-OC$_2$H$_4$OH; C_{22}-OH (95 : 5)	288.49	43.3 42.0*	30.0 (40.8)	43.2 (48.2)	2.60	7.82	10.42
C_{16}-OC$_2$H$_4$OH; C_{22}-OH (50 : 50)	306.53	61.7 57.0*	44.5	62.5 (64.8)	8.30	2.20	10.50
C_{16}-OC$_2$H$_4$OH; C_{22}-OH (5 : 95)	324.57	69.3 67.5*	62.5	(73.7)	—	—	15.30
C_{16}-OC$_2$H$_4$OH; C_{22}-OH (1.99)	326.17	70.2 69.5*	64.1	(74.9)	—	—	16.10
C_{16}-OH; C_{22}-OC$_2$H$_4$OH (99 : 1)	243.76	49.4	40.8 (48.0)	50.3 (54.2)	4.94	6.68	11.62
C_{16}-OH; C_{22}-OC$_2$H$_4$OH (95.5)	248.90	47.8	42.7	(52.8)	—	—	14.07
C_{16}-OH; C_{22}-OC$_2$H$_4$OH (50 : 50)	306.53	52.0±1.0	43.7 (48.9)	—	—	—	11.75
C_{16}-OH; C_{22}-OC$_2$H$_4$OH (5 : 95)	364.23	61.7	41.2 (48.5)	57.3 (67.5)	4.44	10.93	15.37
C_{16}-OH; C_{22}-OC$_2$H$_4$OH (1 : 99)	369.41	63.5	42.7 (48.8)	61.6 (68.3)	2.84	10.50	13.34
C_{22}-OC$_2$H$_4$OH (100)	370.64	64.2	44.0 (50.3)	62.7 (67.7)	3.09	10.50	13.59

*Starting of the softening.
**Value obtained by keeping the rate of heating 0.5°C/min. Single compound values have been taken from ref. 1.

ted $\triangle H_t$ and $\triangle H_f$ values are presented in Table 1. The results show that upto 5 mole percent addition of each component to another, the fusion and transition temperatures decrease. For the equimolecular mixture (curve 3), the solid phase transition is initiated at 44°C and is extended upto 62°C suggesting that the formation of α-phase (hydrocarbon chain is vertical to the plane of the end-group and rotating) is facilitated even at 44°C and it prolongs to the fusion point.

The lowering of the transition and fusion temperatures for curves 1 and 2 is accompanied by a decrease in $\triangle H_t$ and $\triangle H_f$. Further, with the addition of C_{22}—OH to C_{16}—OC$_2$H$_4$OH, $\triangle H_t$ increases and at equimolecular proportion it is nearly four times the $\triangle H_f$ value. The larger $\triangle H_t$ value indicates higher degree of molecular alignment (orientation) in this mixture probably due to chain-chain and polar-polar group interactions. It may be noted that with 1 % addition of C_{16}—OC$_2$H$_4$OH to C_{22}—OH,
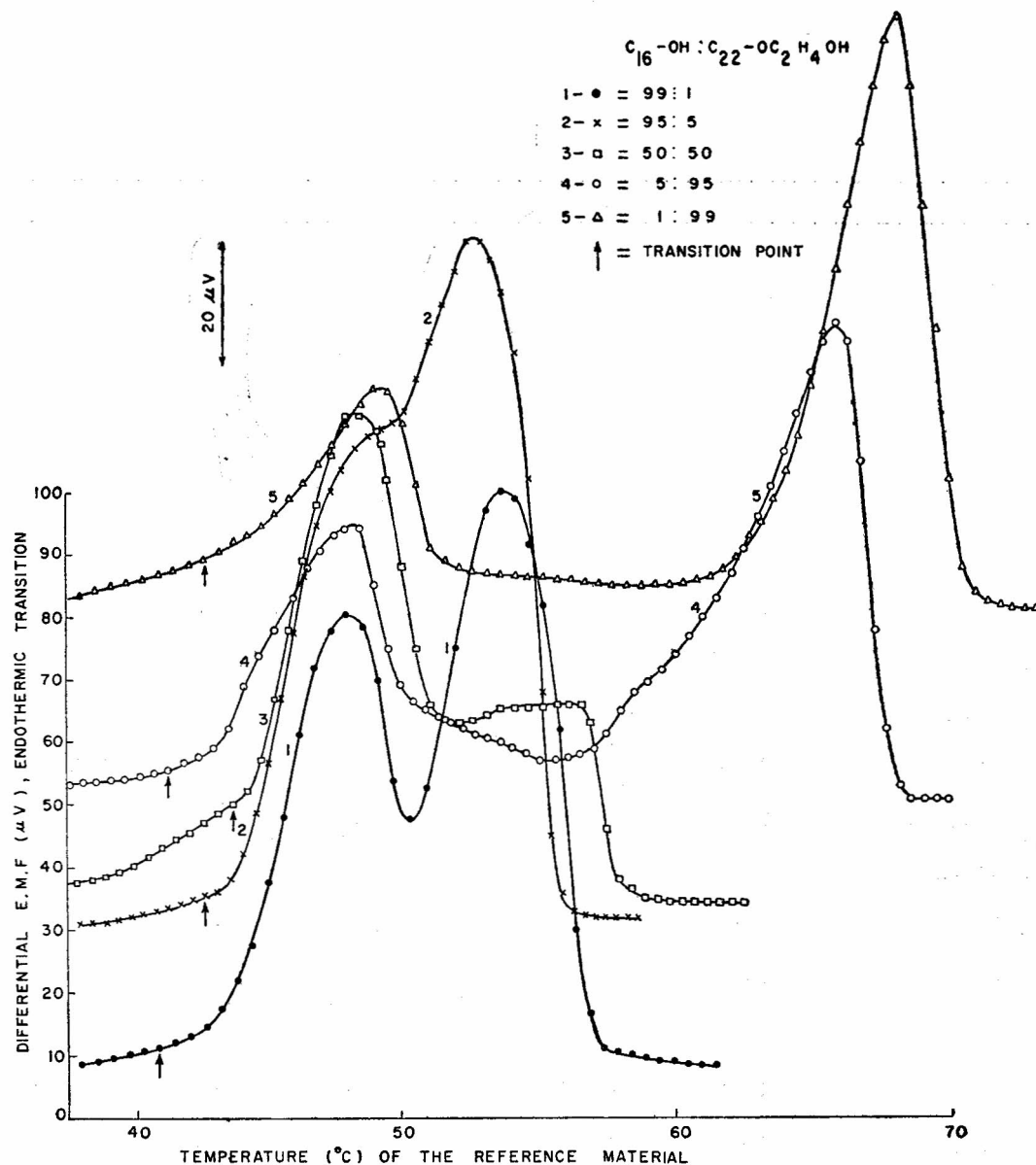
Fig. 2 — DTA curves for the mixture of C_{16}—OH and C_{22}—OC_2H_4OH in various proportions, heating rate = 1°C/min.

the $\triangle H_F$ (16.1 kcal/mol) is higher than that of the pure C_{22} —OH (15.25 kcal/mol) and with further addition, the value decreases to 10.5 kcal/mol. It appears that the compound with extended polar groups, even though present in smaller quantities, effects a closer packing of the alcohol molecules.

C_{16} —OH + C_{22} —OC_2H_4OH — The DTA curves for mixtures of C_{16} —OH and C_{22} —OC_2H_4 OH are shown in Fig. 2. Except for curve 2, the transition and fusion peaks are more pronounced than those in the cases of earlier two mixtures studied. The values corresponding to these peaks and related thermodynamic quantities are presented in Table 1. On the addition of 1 mole percent of C_{22} —OC_2H_4 OH to C_{16} —OH, the transition temperature of C_{16} —OH decreases by 1.1°C, while fusion temperature decreases only by 0.2°C. However, the addition of

5 mole percent of C_{22} —OC_2H_4OH increases the transition temperature. In curve 3, the transition peak is predominant and the fusion peak is relatively obscure, suggesting that the solid phase transition introduces a molecular packing similar to that in liquids. Hence, in this mixture, probably, α-phase predominates even at lower temperatures as seen in curve 3 of mixture C_{16}—OC_2H_4OH+C_{22} —OH (Fig. 3). The transition and fusion temperatures of C_{22} —OC_2H_4OH are lowered by the addition of 1 and 5 mole percent of C_{16} —OH.

With the addition of 1 mole percent of C_{22}—OC_2H_4 OH to C_{16} —OH, the $\triangle H_F$ value decreases by 1.5 kcal/mol whereas addition of 5 mole percent C_{22}—OC_2H_4OH increases the $\triangle H_F$. The equimolar proportion gave $\triangle H_F$ value less than those of the pure components. Similar decrease and increase
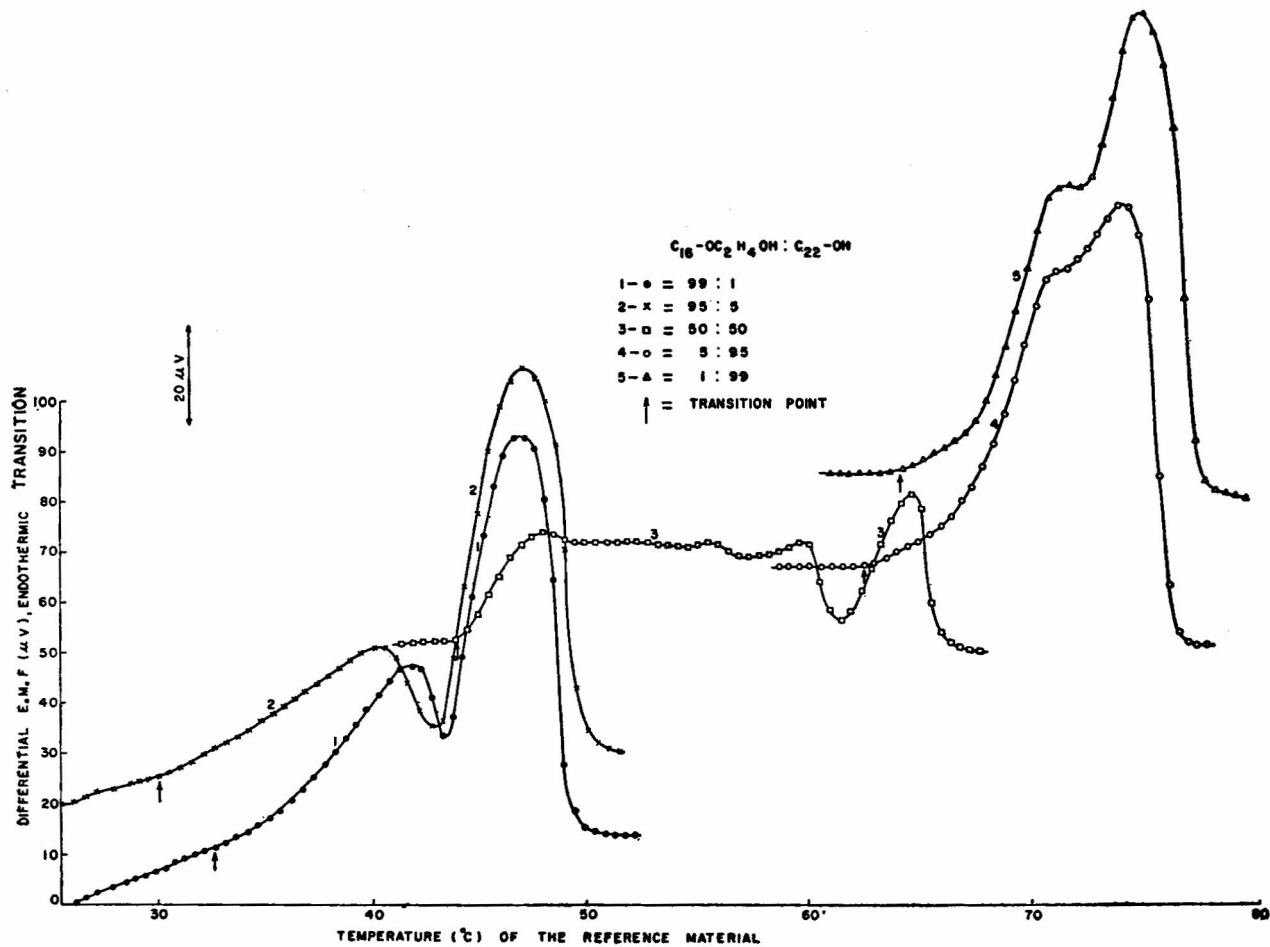
Fig. 3 — DTA curves for the mixture of C_{16}—OC_2H_4OH and C_{22}—OH in various proportions, heating rate = 1°C/min.
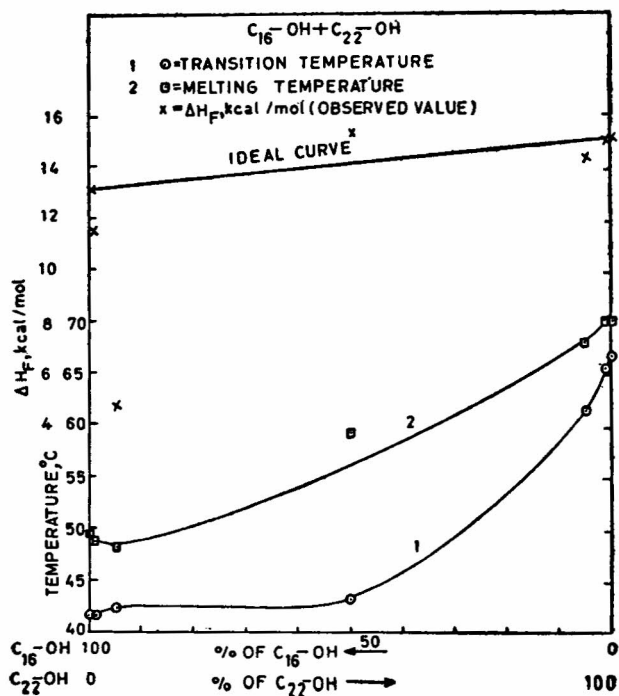

Fig. 4 — Plots of increased molar concentration of C_{16}—OH in C_{22}—OH against transition and fusion temperatures, and total heat of fusion ($\triangle H_F$).

in $\triangle H_t$ values have been observed when 1 and 5 mol percent of C_{16} —OH are added to C_{22} —OC_2H_4OH.

To compare the nature of the curves, it is necessary to ascertain the phase behaviour exhibited by the above mixtures. In Fig. 4 are shown the plots of the molar concentrations of C_{16} —OH and C_{22} —OH against transition and fusion temperatures and $\triangle H_F$. All the curves indicate that Rault's law of ideal solution is not applicable. The formation of any intermolecular complex cannot also be stipulated. As observed by Kolp and Lutton[5] for C_{16}— and C_{18}—OH mixtures, most of the mixtures appear to form solid solutions. As the percentage of one component increases in the mixture, the softening range increases as observed in the capillary method of determining the melting points (Table 1). This is maximum when the mixtures are in equimolecular proportions so that the exact determination of melting point becomes difficult.

DTA data of the studied mixtures indicate that mixtures of same polar groups with different chain lengths have relatively stronger molecular packing whereas mixtures of extending polar group and different chain lengths have loose lattice packing. However, their molecular orientations and structural rigidities depend much upon chain-chain, chain-polar and polar-polar group interactions. Mixtures appear to form homogenous solid solutions.

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