*Journal of Thermal Analysis, Vol. 11 (1977) 61–69*

# PROPERTIES OF MOLTEN ALKALI METAL TRIFLUOROACETATES

## PART I. STUDY OF THE BINARY SYSTEM $CF_3COOK-CF_3COONa$*

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(Received August 30, 1976)

The $CF_3COOK$-$CF_3COONa$ phase diagram was studied by DTA between 100% and 50 wt.% $CF_3COOK$; the thermal decomposition of $CF_3COONa$-rich samples prevents the complete determination of the phase diagram. Two eutectics were found: $E_I$ at 89.5 wt.% $CF_3COOK$ and $E_2$ at 62 wt.%, with melting points at 122–123° and 112–113°, respectively, representing a temperature approximately 30° lower than the m. p. of pure $CF_3COOK$ (140.5°). The presence of a compound between these two eutectics is not formally established, but is probable at about 85 or 87 wt.% $CF_3COOK$, melting at 124–125°. DTA has shown that the fused mixtures solidify into a metastable state, the phase diagram of which presents a labile eutectic at 75 wt.% $CF_3COOK$, melting at 88°.

The thermal instability of fused organic salts, especially molten alkali metal carboxylates, considerably restricts the potential use of these ionic liquid media. However, the decomposition of carboxylates can be limited by working in a dry and inert atmosphere and by excluding impurities such as hydroxy ions and transition-metal cations [1–3]. The determination of phase diagrams is an important part of investigations in the field of molten organic salts, and many binary and ternary systems have been indexed [4, 5].

In particular, the sodium and potassium salts of trifluoroacetic acid have been studied in some detail. $CF_3COONa$ decomposes as it melts, at 200–205° [1, 6, 7]; $CF_3COOK$ melts at 135–137° and decomposes above 145° [1, 6].

In this work, the phase diagram of the system $CF_3COOK-CF_3COONa$ has been determined, in order to find mixtures melting at lower temperatures than the pure salts and thus showing a larger range of thermal stability in the molten state.

## Experimental

### *Preparation of salts*

Potassium and sodium salts were prepared by neutralizing aqueous solutions (5 N) of trifluoroacetic acid (Merck, for synthesis) with the corresponding alkali metal carbonates (Merck, G. R.). The solutions were then evaporated under

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* This paper is based on part of the Dissertation (No. 1721) of R. Dallenbach, University of Geneva.

vacuum for several hours. The salts were recrystallized from an ethanol–chloroform mixture (Merck, G. R.), filtered and dried for at least 48 hours under vacuum ($10^{-3}$ mm Hg) at 50°. The storage and manipulations were done in dry air, in a glove box.

### *Differential thermal analysis (DTA)*

Preliminary experiments have shown that alkali trifluoroacetate mixtures could not be melted directly in the DTA crucibles. To homogenize the melt, the temperature must be held above the m. p. for a long time, causing a too important thermal decomposition. Therefore, to obtain the adequate homogeneous mixtures, 10 – 25 g of sodium and potassium trifluoroacetates in proper ratio were pre-melted under nitrogen (N45) in a Pyrex apparatus. This allowed visual observations and also the recording of the temperature of the mixture against time during its slow cooling (1 – 2° $\text{min}^{-1}$) by stirring and initiating the crystallization. A sample was taken by dipping a Pyrex rod into the homogeneous melt, and quickly taking it out. By this means, 50 – 100 mg of crystallized substance was collected onto the rod and used after pulverization for differential thermal analysis (DTA).

The DTA measurements were carried out with an apparatus constructed in our laboratory. The specimen-holder assembly consisted of a cylindrical aluminium block, into which were fitted two alumina sheaths isolating the Chromel-Alumel thermocouples. The sample and reference holders were set on the differential thermocouple and the temperature thermocouple was placed under the reference material. The $T$ and $\Delta T$ signals were recorded with a potentiometric recorder. A quartz tube covering the specimen-holder assembly enabled operating under vacuum or inert atmosphere. The mobile furnace temperature was controlled manually by a variable transformer.

For DTA, the following conditions were applied: sample and reference ($Al_2O_3$) weight: 10 – 20 mg; crucible: aluminium; heating rate: 3.5° $\text{min}^{-1}$; cooling rate: 5° $\text{min}^{-1}$; atmosphere: $N_2$, 10 ml $\text{min}^{-1}$.

The temperatures are given within an accuracy of $\pm 0.5°$. The heating was stopped immediately after the melting peak in order to avoid decomposition of the samples, which were submitted to at least three consecutive heatings.

### *X-ray diffraction*

Powder Debye–Scherrer patterns were established with a Guinier–de Wolff camera (Nonius). The mixtures were obtained from sampling during thermal pretreatment under cooling, and are therefore identical to those studied by DTA in the first heating. The exposures were taken over a 4 h period under operating conditions of 30 kV and 30 mA for Cu$K_\alpha$ radiation. These experiments were carried out in order to try to determine the nature of some of the more noteworthy compositions of the binary $CF_3COOK - CF_3COONa$ diagram. Therefore only the appearance and disappearance of some characteristic lines were observed.

## Results

### *Results obtained on heating*

The melting temperatures of $CF_3COOK$ and $CF_3COONa$ are 139.5 – 141.5° and 206 – 208°, respectively. We did not notice any polymorphic transformation between 25° and the melting points. For the sodium salt, decomposition takes place during melting and this was observed in the DTA curves as an exothermic peak coupled with the melting peak. For the potassium salt, the deviation from the baseline corresponding to the beginning of decomposition is noticeable only above 150 – 160°.

Figure 1 represents a series of DTA peaks obtained with $CF_3COOK$ and some binary $CF_3COOK$-rich mixtures. The mixtures containing 97, 94, 92 and 91 wt.% $CF_3COOK$ show two characteristic effects due to eutectic melting and non-isothermal melting, corresponding to the range between the solidus and liquidus lines. For 90.5, 90 and 89.5 wt.% $CF_3COOK$ mixtures, a single peak

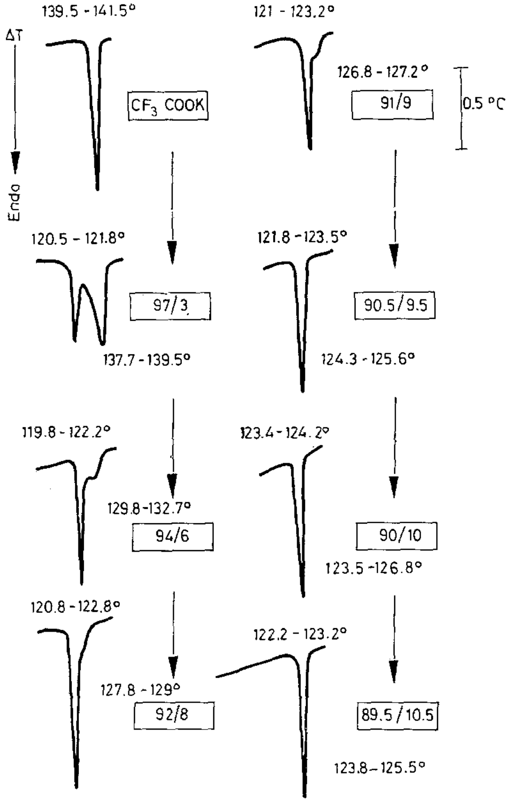

Fig. 1. DTA heating curves of $CF_3COOK$ and $CF_3COOK$–$CF_3COONa$ mixtures (heating rate: 3.5° $min^{-1}$). Compositions in wt.% $CF_3COOK/CF_3COONa$

was observed. We could not observe two thermal effects, because either they were too close together or only a single phase was present. For these mixtures, we have indicated the extrapolated onset and maximum peak temperatures, the latter corrected with respect to the baseline. From the mean values of these temperatures, the *T–X* diagram was constructed (Fig. 2). In this Figure, the results obtained from the cooling curves (rate: 1 – 2° min$^{-1}$) determined during the sampling are also shown. This diagram has been studied only to 50 wt. % $CF_3COOK$, as the thermal decomposition of samples richer in the sodium salt disturbs the measurements. The diagrams determined by these two methods are in good agreement; in general the difference does not exceed ±1°.

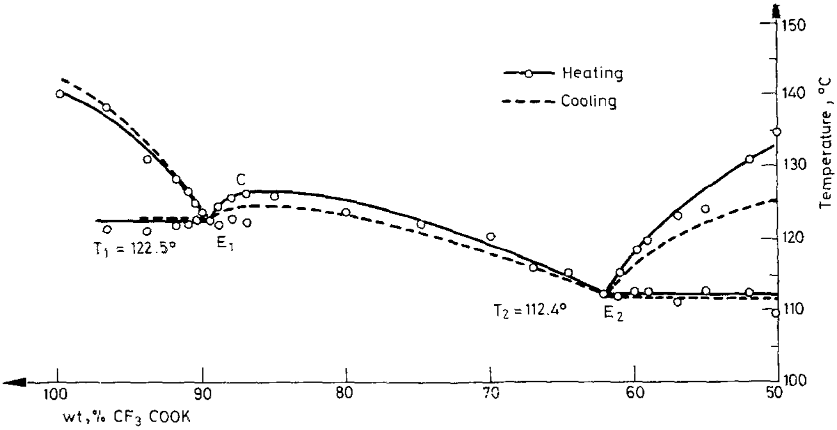

Fig. 2. Phase diagram of the $CF_3COOK$–$CF_3COONa$ system determined by DTA, and previously applied thermal treatment (cooling rate: 1 – 2°min$^{-1}$)

This binary diagram shows two minima determined as the intersecting point of the liquidus and eutectic lines. The first minimum ($E_1$) corresponds to a composition of 89.5 wt. % $CF_3COOK$ ($T_1$: 122.5°), while the second ($E_2$) lies at 62 wt. % $CF_3COOK$ ($T_2$: 112.4°). Between these two minima, the liquidus line was plotted by taking the temperatures corresponding to the peak maxima. A very flat maximum (*C*) was noticed, the composition of which is poorly defined; it probably lies at about 85 – 87 wt. % $CF_3COOK$ and would correspond to a weakly-stable compound $5\,CF_3COOK \cdot CF_3COONa$ or $6\,CF_3COOK \cdot CF_3COONa$, melting at 124 – 125°. It should be mentioned that eutectic peak was never observed within this part of the diagram; the same phenomenon was also found in the cooling curves.

The main lines of the potassium and sodium trifluoroacetate X-ray patterns are indexed in Table 1; their intensities were estimated visually. The $CF_3COONa$ X-ray pattern is diffuse and the intensity of the lines is very weak. However, $CF_3COOK$ presents many lines, the most important corresponding to the pattern determined by Watt and Muga [8].

Table 1

Interreticular distances (d, Å) relating to sodium and potassium trifluoroacetates

| Alkali metal salt | Strong I | Medium I | Weak I | Remarks |
|---|---|---|---|---|
| $CF_3COONa$ | — | — | 4.35 | All lines are very weak (sequence between 4.2 and 3.4) |
| $CF_3COOK$ | 3.45 | 5<br>3.78 (2)<br>3.18<br>2.29<br>2.22<br>2.16<br>2.15 | 3.36<br>2.52<br>2.48<br>2.36<br>etc. . . . | One strong line and numerous medium and weak lines |

For the mixtures, X-ray patterns are more difficult to interpret as the sodium salt concentration increases. Nevertheless, we noticed the evolution of some lines corresponding to the different phases. The intensity of primary phase lines ($CF_3COOK$, d = 3.45; 5; 3.78; etc.) decreases with the $CF_3COOK$ concentration and these lines disappear completely at about 80–85 wt.% $CF_3COOK$. With the disappearance of these lines, we observed the appearance of a secondary phase at 97 wt.% $CF_3COOK$, its importance increasing with the sodium salt concentration.

The intensity of secondary phase main lines (d = 3; 3.55) reaches a maximum at about 80–85 wt.% $CF_3COOK$ and this coincides with the disappearance of the primary phase. This qualitative interpretation of the X-ray patterns indicates that the secondary phase coincides well with that of compound C (85–87 wt.%) determined by DTA.

### *Results obtained on cooling*

Two phenomena were observed on cooling, but the curves do not correspond to those obtained on heating. The temperature of the first peak decreases logically with the diminution of the potassium salt concentration, even though the second peak lies at an approximately constant temperature, i.e. 65–70°. However, the latter does not indicate the solidification of the eutectic $E_1$, for when this composition was reached evidence of two thermal effects was also noted.

The difference of the temperatures of the exothermic phenomena observed on cooling is rather appreciable, ranging from 5 to 10°. These results are indicated in diagram $T$–$X$ (II) (Fig. 3). In all cases, the highest temperature was chosen, as it is likely to be the nearest to the crystallization temperature without undercooling. In this diagram, it was noted, starting from the potassium salt, that the curve corresponding to the first thermal effect agrees well with the liquidus curve obtained on heating down to 90 wt.% $CF_3COOK$. In effect, it lies at a lower temperature, which is quite normal taking into account the undercooling. From this composition, the curve keeps on decreasing to 75 wt.% $CF_3COOK$, where it reaches the minimum value of 68° ($M_1$). This temperature corresponds to the second thermal effect temperature, noticeable below 92 wt.% $CF_3COOK$. Below 75 wt.% $CF_3COOK$ a single phenomenon was observed, the temperature of which increases with the concentration of the sodium salt. We could then construct the second branch of the liquidus obtained on cooling.

*Results obtained on successive heatings*

It must be pointed out that these results were not reproducible and were never obtained on first heating. It would also appear that the presence of thermal effects on subsequent heatings is connected with a phenomenon occurring on cooling under DTA conditions. The DTA curves show two endothermic effects. The first peak is narrow, its surface increases to 75 wt.% $CF_3COOK$ and its temperature is constant, 86–88°. The second thermal effect appears as a very wide peak, the surface and temperature of which decrease to 85 wt.% $CF_3COOK$. The 75 wt.% $CF_3COOK$ mixture presents a single peak at 88° ($M_2$); then two peaks were again observed at 70 wt.%, at 87° and 101°, respectively. We have indicated the values of these temperatures in diagram III (Fig. 3).

The $CF_3COOK-M_2$ branch is first superimposed on the $CF_3COOK-E_1$ branch of the diagram determined previously on heating but then goes on to $M_2$, where a horizontal line at 88° is indicated; the branch then goes up to the eutectic $E_2$.

During some heatings, we noticed the presence of a sharp exothermic peak at 90–92°, which is generally associated with an endothermic peak at 82–88°. The

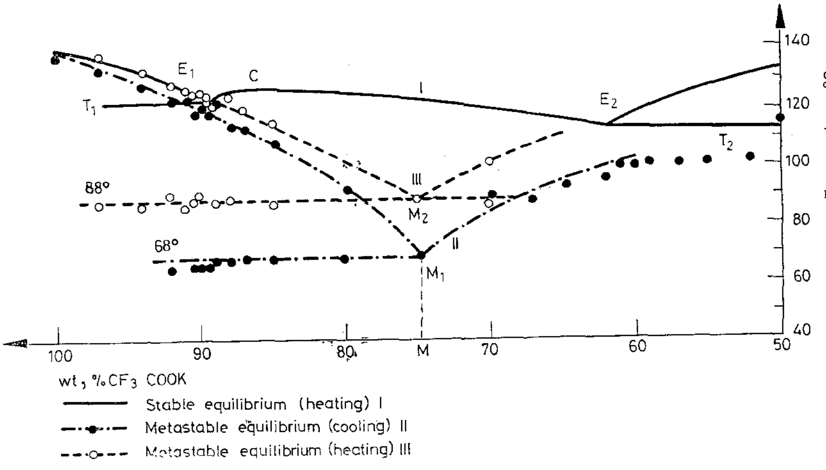

Fig. 3. Phase diagram of the $CF_3COOK$–$CF_3COONa$ system determined by DTA on cooling and on successive heatings

presence of this peak is very important, because in all cases it modifies the shape of the DTA curves. With a further increase of temperature, the DTA curves then correspond to the equilibrium diagram normally obtained on heating. In order to illustrate this behaviour, a sequence of heating curves of a 92 wt.% $CF_3COOK$ mixture is represented in Fig. 4.

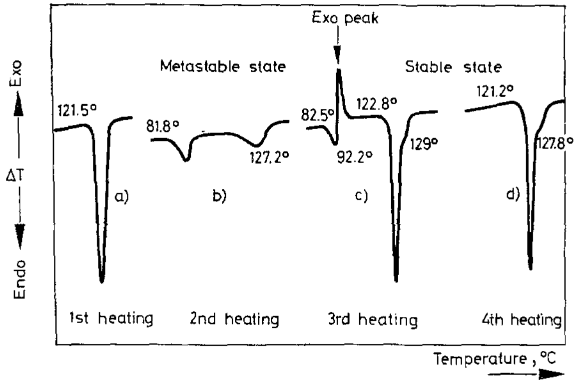

Fig. 4. Successive DTA heating curves of a 92 wt.% $CF_3COOK$ mixture (heating rate: 3.5° $min^{-1}$)

In our opinion, the exothermic peak indicates the transition from a metastable state, obtained on cooling to a stable state corresponding to the $CF_3COOK-E_1$ $CE_2$ diagram, as determined by previously applied thermal treatment and DTA under particular conditions. The exothermic peak temperature is very reproducible, but its surface area varies considerably, according to the number of heating cycles to which the same sample was subjected. We explained this difference by the fact that the metastable state spontaneously and slowly transforms into the stable form at room temperature. If the heating is stopped after the appearance of the exothermic peak and the sample is allowed to cool, subsequent heating gives the peaks corresponding to the stable diagram, as shown, for example, in curve d) in Fig. 4.

## Discussion

With DTA, we were able to show that molten $CF_3COOK-CF_3COONa$ mixtures give two solid phases on cooling. One of the liquid-solid equilibria is illustrated by diagram I (Figs 2 and 3), corresponding to the DTA curves obtained on first heating and on subsequent heating, generally carried out several hours after cooling or when the exothermic peak at 92° was present. This diagram also corresponds to that determined by previously applied thermal treatment. It is thought that this diagram relates to the stable equilibrium state of the $CF_3COOK-CF_3COONa$ mixtures, as it was always obtained when undercooling was suppressed by initiating the crystallization and when the exothermic peak was observed by DTA on heating, which corresponded to the transition from an upper to a lower energy state.

This diagram includes the following points: eutectic $E_1$, at 89.5 wt. % $CF_3COOK$, melting at 122 – 123° ($T_1$); eutectic $E_2$, at 62 wt. % $CF_3COOK$, melting at 112 – 113° ($T_2$); a compound C, the composition of which is not clearly defined, but which probably lies at 85 or 87 wt. % $CF_3COOK$, melting at 124 – 125°.

It appears from this study that the $CF_3COOK – CF_3COONa$ mixtures near a composition of 62 wt. % $CF_3COOK$ offer the greatest interest for the application of organic molten media, since the melting point (112 – 113°) is lower by about 30° than the melting point of pure $CF_3COOK$ (139.5 – 141.5°). Work is at present being carried out on the thermal decomposition of alkali metal trifluoroacetates and some of their mixtures.

The diagram II (Fig. 3) obtained on cooling shows that part of the liquidus lies close to that determined on heating; nevertheless, the branch continues beyond $E_1$. For instance, if we consider the behaviour of a fused mixture between pure salt and $E_1$, $CF_3COOK$ crystals must segregate from the liquid phase in the absence of a solid solution. When the liquid reaches the eutectic composition $E_1$ and does not crystallize from undercooling, the potassium salt continues to segregate and the composition of the liquid follows the branch $E_1M_1$ and reaches the composition $M_1$, corresponding on the diagram to an invariant point at 68°. When such a sample is immediately reheated and the exothermic peak is absent, we obtain diagram III (Fig. 3), the shape of which is similar to the diagram determined on cooling, although there is a shift in temperature. A metastable invariant point $M_2$ was found at 88°. By stopping the heating or cooling after the appearance of thermal effects in relation to diagrams II and III, we found a perfect correspondence of the peaks relating to these two diagrams, representing therefore a single phenomenon, that is to say a metastable equilibrium state. The thermal effects should be superimposed. Under DTA conditions, we always obtained such an equilibrium on cooling, due to lack of stirring and initiation of crystallization. In this case, the $CF_3COOK$ seeds form fairly easily, to enable this salt to crystallize as the temperature decreases. However, the viscosity of the residual liquid increases so much that the rate of formation of the crystals $E_1$ and C drops to almost zero and the system then evolves along the $CF_3COOK – M_1$ curve.

This unexpected behaviour arouses some interest in the study of the properties of this metastable solid state, especially as regards the nature of the labile eutectic ($M$) for a 75 wt. % $CF_3COOK$ composition.

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Thanks are due to Professor R. Monnier and Dr. J. J. Duruz for useful discussions.

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Résumé — Le diagramme de phases $CF_3COOK$-$CF_3COONa$ a été établi par ATD entre $CF_3COOK$ et le mélange à 50% poids; la décomposition thermique des échantillons riches en $CF_3COONa$ empêche la détermination complète du diagramme de phases. On observe deux eutectiques: $E_1$ à 89.5% poids en $CF_3COOK$ et $E_2$ à 62% poids, fondant respectivement à 122—123° et 112—113°, ce qui représente un abaissement d'environ 30° C par rapport au P. F. de $CF_3COOK$ pur (140.5°). L'existence d'un composé entre ces deux eutectiques n'a pu être montrée formellement. Il se situe vraisemblablement vers 85 ou 87% poids en $CF_3COOK$ et fond à 124—125°. L'ATD a montré que les mélanges fondus se solidifient dans un état métastable, dont le diagramme de phases présente un eutectique labile à 75% poids en $CF_3COOK$ fondant à 88°.

Zusammenfassung — Das $CF_3COOK$—$CF_3COONa$ Phasendiagramm wurde mittels DTA, zwischen 100 und 50 Gew.% $CF_3COOK$ untersucht; die thermische Zersetzung $CF_3COONa$-reicher Proben macht die Bestimmung des vollständigen Phasendiagramms unmöglich. Zwei Eutektika wurden gefunden: $E_1$ bei 89.5 Gew. % $CF_3COOK$ und $E_2$ bei 62 Gew.%, mit den entsprechenden Schmelzpunkten bei 122—123° und 112—113°, welche bei um etwa 30° niedrigeren Temperaturen liegen als der Schmelzpunkt des reinen $CF_3COOK$ (140.5°). Die Existenz einer Verbindung zwischen diesen beiden Eutektika wurde zwar nicht genau bewiesen, sie liegt aber wahrscheinlich bei etwa 85 oder 87 Gew.% $CF_3COOK$ und schmilzt bei 124—125°. Mittels der DTA konnte nachgewiesen werden, daß die geschmolzenen Gemische in einen metastabilen Festkörperzustand übergehen, dessen Phasendiagramm ein labiles Eutektikum bei 75 Gew.% $CF_3COOK$ mit einem Schmelzpunk bei 88° aufweist.

Резюме— С помощью ДТА и ТА изучена фазовая диаграмма смеси $CF_3COOK$—$OF_3COONa$ с содержанием $CF_3COOK$ между 100 и 50 вес.%. Термическое разложение образцов с богатым содержанием $CF_3COONa$, мешает полному определению фазовой диаграммы. Было обнаружено две эвтектики: $E_1$ при содержании $CF_3COOK$ 89,5 вес.% и $E_2$—62 вес.% с точками плавления соответственно при 122—123° и 112—113°, представляющие температуру приблизительно на 30° ниже, чем т. пл. чистого $CF_3COOK$ (140,5°). Наличие какого-либо соединения между этими двумя эвтектиками формально не установлено, но, возможно, оно существует при содержании $CF_3COOK$ 85 или 87 вес.% и плавится при 124—125°. ДТА показал, что расплавленные смеси затвердевают до метастабильного состояния, фазовая диаграмма которого представляет лабильную эвтектику при содержании $CF_3COOK$ 75 вес.% с плавлением при 88°.