Free Energy Measurements of Sodium Chloride in Fused Mixtures with the Alkaline Earth Chlorides

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For systems of the type sodium chloride alkaline earth chloride the partial molar free energies of mixing and partial molar entropies of mixing of sodium chloride have been measured. The data were obtained from electromotive force measurements of galvanic cells of the type

$$Cl_2(g) \mid NaCl(l) \mid Glass-membrane \mid (Na-M)Cl(l) \mid Cl_2(g)$$

where M is Mg, Ca, Sr, and Ba.

In two previous papers by Førland and Østvold 1,2 the liquid junction potential

HROCI. Present work

— FINOCI. Kleppa et al.

• GROCI. Neil et al.

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• All Present work

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• All

Fig. 1. Excess partial enthalpies of mixing of sodium chloride in mixtures with alkaline earth chloride.

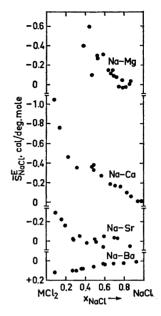


Fig. 2. Excess partial entropies of mixing of sodium chloride in mixtures with alkaline earth chloride.

was discussed for galvanic cells of the type mentioned above. The junction potential was found to be in the order of magnitude 10^{-3} % of the total potential. This is well within experimental error. The emf values measured by this method will therefore give the partial free energy of sodium chloride in the mixture directly. A summary of the results is given in Figs. 1 and 2 where excess enthalpies and entropies are plotted as functions of composition of the mixture. It can be seen from Fig. 1 that the agreement between partial molar enthalpies calculated from integral enthalpies taken from a work by Kleppa and McCarty and partial molar enthalpies from this work is fairly good, while the partial molar free energies given by Neil et al.4 differ markedly from our results.

An extensive discussion of this work will later appear in this journal. Work on galvanic cells of the type mentioned above with other alkali-alkaline earth-chloride mixtures is in progress.

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Cholesterol in the Milk of Cows on Normal and Protein-free Feeds

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The presence of cholesterol in milk has not attracted a great deal of attention; there have been a number of estimations of the concentration of cholesterol in milk and most of the figures fall in the range 11-14 mg per 100 ml milk, equivalent to about 0.35% of milk fat. A small proportion only is esterified. Cholesterol is known to account for the major part of the sterol fraction of butterfat: the identity of the other components, except for lanosterol, has not been established.

The concentration of cholesterol in the lipid of isolated fat-globule membrane material ³ and in the lipid found associated with the milk proteins ⁴ is high, and cholesterol other than that found in the fat globules amounts to some 14 % of the total milk cholesterol, ¹ so that its concentration in the bulk fat phase is relatively low: butter or butterfat figures average about 250 mg cholesterol per 100 g fat.

Only few investigations on the dependence of the milk cholesterol level on feeding, season, stage of lactation, and breed have been reported. Nataf et al. found no seasonal differences, and others have found neither breed nor seasonal differences, though some lactation trends have been noted.

Recently a significant role in milk fat synthesis has been indicated for cholesterol, and it has been proposed that cholesterol ester is an agent in the transfer of fatty acids to form the triglycerides of milk fat.⁶ Later the same authors found an active system in freshly-secreted milk capable of synthesising glyceride from fatty acid.⁷ Thus it appears that cholesterol is secreted as part of milk just as are the other factors responsible for the synthesis of milk fat.

Virtanen has described a series of experiments which have shown that it is possible to maintain the milk production of dairy cows at a relatively high level over a period of several years with a feed in which the protein has been completely replaced by urea and ammonium salts. The feed consists basically of purified carbohydrates (starch, cellulose and sucrose). Small quantities of vegetable oil (35-130 g per day) have been included in the feed; thus the fat intake of the test cows is low. As part of these experiments milk cholesterol values were determined over a period of three years and compared with those of samples taken from cows of the same breed (Ayrshire) on normal feed.

Experimental. Milk fat was determined by the Röse-Gottlieb or Gerber methods and Röse-Gottlieb fat was used for cholesterol determination. Total cholesterol was found by saponification of the fat, precipitation of the cholesterol with digitonin and ferric chloride-sulphuric acid colorimetry. The method, free of interference from lanosterol, was found to give reliable results. The same colorimetric procedure was applied directly to the cholesterol ester fraction separated by column chromatography on silica gel.

Results and discussion. Milk samples were collected from eight farms with herds on normal feed. Silage feed gave a mean value of 300 mg cholesterol per 100 g milk fat, hay feed 320, hay-roots 340, and pasturage 330. There were no significant differences among the various winter feeds: the overall means (93 samples) were 317 \pm 4 (standard error) mg cholesterol per 100 g fat, 137 \pm 2 mg per kg milk, and cholesterol ester 5 % of the total cholesterol.

The mean figures for the five cows receiving the protein-free feed were 400, 370, 480, 435, and 435 mg cholesterol per 100 g milk fat; the overall means (85 samples) were 413 \pm 6 mg per 100 g fat, 231 \pm 5 mg per kg milk, and cholesterol ester 6 % of the total.