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INFLUENCE OF TEMPERATURE AND COMPOSITION ON SOME PHYSICAL PROPERTIES OF MILK AND MILK CONCENTRATES: V,* ELECTRICAL CONDUCTIVITY

F. FERNÁNDEZ-MARTIN, and P.D. SANZ

Instituto del Frío (CSIC), Ciudad Universitaria, 28040 Madrid, Spain

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Electrical conductivity was determined at 1 kHz, in the temperature range of 5–75 °C on 3 families of milk concentrates including 28 samples, up to about 40% solids content. Viscosity was a major cause of conductivity variation and a relationship between both physical properties is established. Temperature and compositional effects were studied and parametric equations relating conductivity to these parameters are given. A nomogram is presented for easier prediction of milk electrical conductivity from temperature and solids content.

Keywords: electrical conductivity, milk concentrates, composition effects, temperature effects, conductivity-viscosity relationship, conductivity prediction.

Electrical conductivity has been proposed as a method of milk quality control in the detection of neutralizing salts, watering and mastitic milk; as a means of monitoring the composition of dairy products under processing, i.e. in the curd-preparation phases of (Emmental) cheese making; in the concentration of sweetened condensed milk or, conversely, as a physical basis for automatic instrumental milk analysis. A very comprehensive review of literature data and applications, with 86 references, has recently been published by Rüegg et al. [1]. On the other hand, conductivity has also been indicated as the control parameter for a number of electrical treatments of milk such as low voltage d.c. electroneutralization of highly acid milks [2, 3], milk pasteurization with electricity by resistive heating at 3000 V [4], or milk sterilization [5]. Obviously, it is in this field that a knowledge of the electrical properties of milk and milk products may play an important role; for instance, in dielectric heating, which has been already applied in pilot scale milk sterilization or in "pasta-filata" cheese making, but from which wider applications may be expected in the dairy industry. Dielectric properties of milk products at radiofrequencies and microwaves will thus be of great interest, but also d.c. electrical conductivity because of its relationship with dielectric losses.

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Experimental

Materials

Commercial sterilized and homogenized whole milk (W1) and skim-milk (S1) and their half and half mixtures (H1) were concentrated in the laboratory by a rotary-evaporator under reduced pressure (30–40 mmHg; 40–50 °C) at different levels up to about 40% solids content. The samples were analysed for fat, lactose and total solids by means of a Milko-Scan 104 (A/S N. Foss Electric, Denmark). Results are given in Table 1, where a degree of concentration is established as the ratio of the solids content of the concentrate to that of the original sample from which it derived.

Table 1

Mean results for fat *(f)*, protein *(p)*, lactose *(l)* and total solids *(s)* in skim-(S), half and half-(H) and whole-(W) milk concentrates. Data in per cent by weight

Degree of concentration	S-concentrates				H-concentrates				W-concentrates			
	f	*p*	*l*	*s*	*f*	*p*	*l*	*s*	*f*	*p*	*l*	*s*
0.5	0	1.54	2.15	4.15	0.90	1.58	2.23	5.10	1.57	1.59	2.20	5.73
1	0.07	3.00	4.19	8.07	1.64	2.95	4.16	9.50	3.24	3.07	4.25	11.07
1.2	0.10	3.40	4.84	9.50	1.92	3.49	4.98	11.24	–	–	–	–
1.3	0.14	3.88	5.55	10.64	–	–	–	–	–	–	–	–
1.5	–	–	–	–	2.61	4.53	6.53	14.46	4.88	4.49	6.36	16.28
2	0.27	6.10	8.66	15.87	3.41	5.93	8.40	18.79	6.53	5.91	8.56	21.64
2.2	–	–	–	–	–	–	–	–	6.98	6.68	9.25	24.10
2.4	–	–	–	–	3.92	7.04	10.15	22.47	–	–	–	–
2.5	0.33	7.28	10.39	20.09	–	–	–	–	–	–	–	–
2.6	–	–	–	–	–	–	–	–	8.52	8.04	11.18	28.53
2.8	–	–	–	–	4.65	8.96	11.79	26.92	–	–	–	–
3	0.39	9.40	12.98	24.15	–	–	–	–	9.60	9.12	12.62	32.87
3.1	–	–	–	–	–	–	–	–	10.07	9.54	13.21	34.42
3.3	0.41	9.88	14.14	26.45	5.55	10.19	14.69	32.53	–	–	–	–
3.5	–	–	–	–	–	–	–	–	11.12	10.66	14.76	38.44
3.6	–	–	–	–	5.90	10.52	14.90	34.17	–	–	–	–
3.8	0.48	11.75	16.76	30.99	–	–	–	–	12.35	11.65	16.13	42.01

Code 0.5 refers to samples obtained by proper dilution with distilled-deionized water from the respective starting ones.

Conductivity

Since previous experimental work showed, as expected [6], that milk electrical conductivity was frequency-independent in the range of 50 Hz to 10 kHz, measurements were made at a single frequency of 1 kHz by means of a digital impedance bridge meter GR 1684 (General Radio Co., USA) coupled to a conductimetric WTW cell, type LDT (Wissenschaftlich Technische Werkstätten GmbH, FRG) provided with a jacket for thermostatic control, which was accomplished within 0.05 °C. The system was calibrated by means of two aqueous solutions of KCl covering the conductivity range of the milk samples.

Viscosity

Determinations were made by a coaxial cylinders viscometer Rheomat RM15 provided with a measuring cell MS–0 (Contraves AG, Switzerland). Shear rates between 40 and 1800 s^{-1} were used and coefficients of dynamic viscosity were calculated by linear regression between shear stress (from viscometric readings) and shear rates. Measurements were carried out under thermostatic control of ±0.05 °C.

Results and discussion

Temperature effects

Experimental mean results of 3–4 samples for each case are given in Figs 1, 2 and 3 for S-, H- and W-concentrates respectively. Preliminary data on skim milk concentrates have been already reported [7].

Early literature but also some recent papers [8] have reported linear relationships for electrical conductivity with temperature. In the investigated temperature range, however, there was a definite non-linear increasing of κ (Sm^{-1}) with increasing temperature t (°C) which was well represented by a quadratic in temperature expression of the type $\kappa = a + bt + ct^2$, whose parameter coefficients a, b, c were obtained by regression methods for each individual sample. The correlation coefficients r yielded values between 0.9994 and 0.9999 and calculated conductivities, represented by full lines in Figs 1, 2 and 3, fitted experimental data with standard deviations, s.d. (n = 15) ranging from 0.002 (H2.1) to 0.009 (S3.3) in conductivity units.

The temperature coefficient of electrical conductivity $\alpha = \frac{1}{\kappa}\frac{d\kappa}{dt}$ (°C^{-1}), also proved to be a function of temperature, decreasing non-linearly with increasing temperature. For W1, whose composition is close to that of normal milk, the corresponding fitted line was $\alpha = (32.5 - 0.57t + 0.0039t^2) \times 10^{-3}$ with $r = 0.9962$ and s.d. (n = 15) = 0.041. For a given temperature α exhibited a linear relationship with solids content s (%) within each series of concentrates, but the slopes of the three series S, H and W were practically the same, i.e. independent of the ratio of fat to solid-nonfat. In the temperature region where mastitis control is normally performed, data were as follows: at 25 °C α increased linearly 0.105×10^{-3} $^{\circ}C^{-1}$ per per cent of solids content *s*; at 30, 35 and 40 °C the respective figures were 0.099, 0.092 and 0.086×10^{-3}.

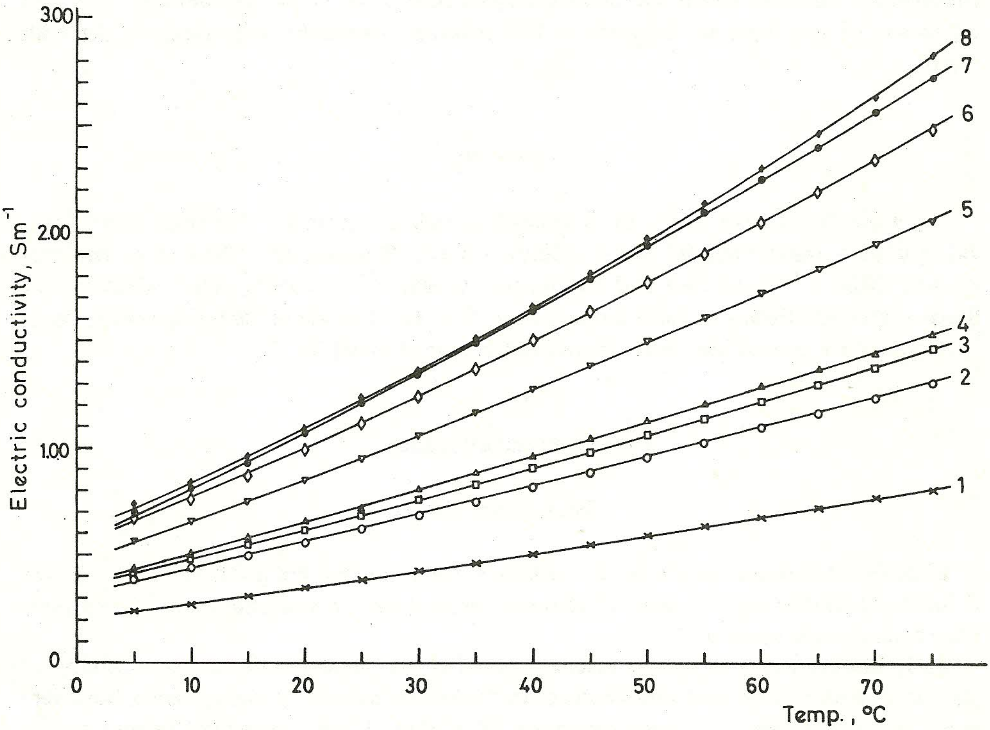

Fig. 1. Effect of temperature on electrical conductivity of skim-milk concentrates; 1: S0.5; 2: S1; 3: S1.2; 4: S1.3; 5: S2; 6: S2.5; 7: S3; 8: S3.3 (S3.8 not shown for sake of clarity)

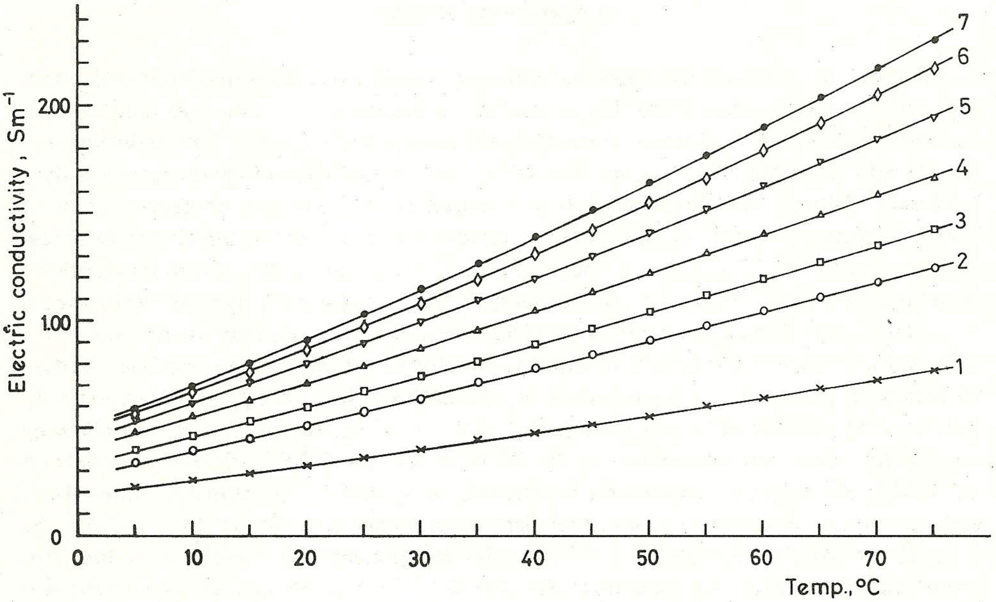

Fig. 2. Effect of temperature on electrical conductivity of half-half milk concentrates. 1: H0.5; 2:H1; 3: H1.2; 4: H1.5; 5: H2; 6: H2.4; 7: H2.8 (H3.3 and H3.6 not shown)

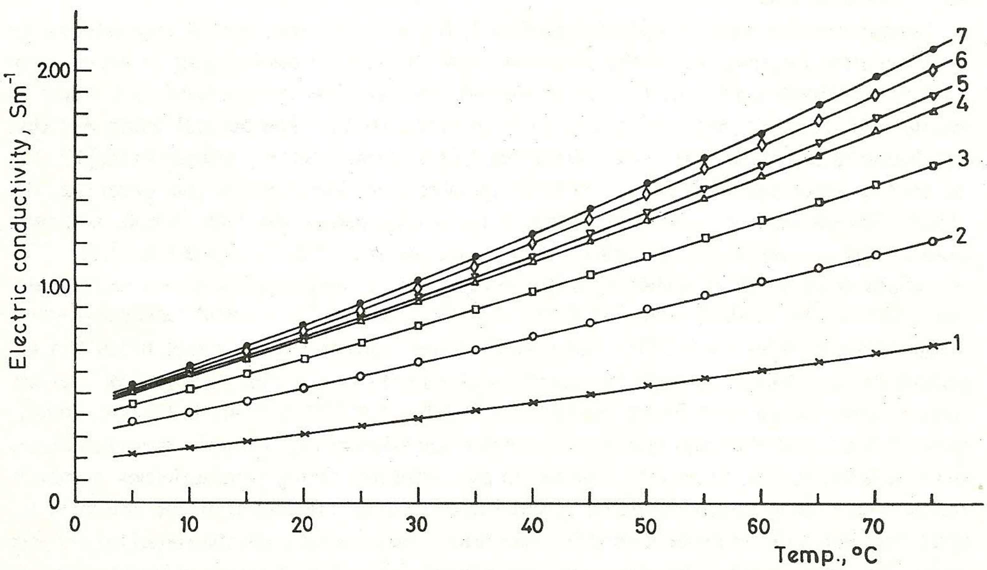

Fig. 3. Effect of temperature on electrical conductivity of whole milk concentrates. 1: W0.5; 2 :W1; 3: W1.5; 4: W2; 5: W2.2; 6: W2.6; 7: W3 (W3.1, W3.5 and W3.8 not shown)

Compositional effects

Variation of electrical conductivity with composition has been investigated by Kats [9], and by Oshima and Fuse [10] in normal, individual cow's milk and quarter milk samples respectively, by means of multiple linear regression models. Kats reported that protein and fat content had the greatest effect on conductivity, which decreased as they increased. Oshima and Fuse established a boundary composition of quarter milk at 7.13% (lactose + protein) or 9.77% (fat + lactose + protein) above which the electrical conductivity at 40 °C was lower than 6.5 Sm^{-1}, while below that figure conductivity raised over 8.0 Sm^{-1}. Moreover, Jackson and Rothera [11] as early as in 1914 reported a strict reciprocity between electrical conductivity and lactose content in quarter cow's milk and in right and left breasts in women. Compositional effects have also been studied by means of multiple linear regression of the present experimental results on conductivity and fat (f%), protein (p%) and lactose (l%) contents of the samples, with the following results for data corresponding to 25 °C ($n = 28$), $\kappa = 0.4069 - 0.0239\,f - 0.0983\,p + 0.1259\,l$, the multiple correlation coefficient being 0.867. The statistical analysis of variance showed that the regression provided a satisfactory description of the data for the 3 types of samples, P = 99.9% (***); the fat component was significant at the level P = 97.5%, the protein component at P = 99.9% (***), but the lactose component was not significant, (P = 50%). Application of multiple linear regression individually to each of the 3 series of concentrates yielded not only different values but also different signs for the parameter coefficients: indicating the lack of foundation of this statistical model for the present case.

Concentration effects are plotted in Figs 4, 5 and 6 as a function of total solids content by using temperature as the parameter (for the sake of clarity, data at every other temperature were omitted). Concentration effects were less pronounced in the case of whole milk concentrates due to the dilution effect of fat. The general trend was that conductivity increased with solid percentage but at a progressively retarded rate [12, 13] so that a maximum and then a definite decreasing in conductivity was observed. Relationships between κ and solids content were established for each sample and temperature as polynomial functions of second degree in s, that is, $\kappa = a + bs + cs^2$. The equations obtained always showed independent terms a very small, their extreme values being 0.001 for H/40°C and 0.036 for W/70°C; the multiple correlation coefficients varied from 0.9935 to 0.9995. Calculated values from these equations fitted the experimental data quite well, as indicated by the solid lines of Figs 4, 5 and 6. The s.d. ranged from 0.006 ($n = 9$) to 0.013 ($n = 10$) for H/10°C and W/10°C, respectively; samples 0.5 being the main contributors to the deviation of experimental from calculated data. It is interesting to note that these samples exhibited actual conductivities (symbols) much higher than those expected (solid lines), due to the fact that the proportional reduction in conductivity produced by the dilution was partially compensated by a higher degree of dissociation. This fact was one reason, from a mathematical point of view, for which the independent term a above mentioned did not get the null value, as it would in the ideal case, i.e. $\kappa = 0$ when $s = 0$.

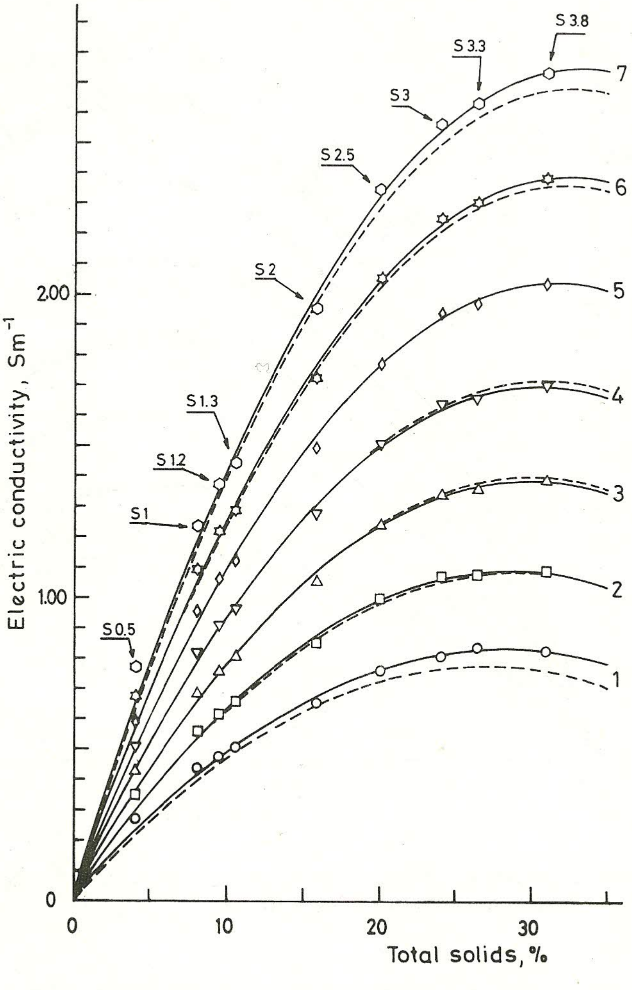

Fig. 4. Effect of concentration on electrical conductivity of skim-milk concentrates. 1: 10 °C; 2: 20 °C; 3: 30 °C; 4: 40 °C; 5: 50 °C; 6: 60 °C; 7: 70 °C

Viscosity effects

The location of the conductivity maximum was difficult to establish due to the diverse and even opposing factors affecting conductivity; apparently it shifted towards higher dry matter contents when moving in the direction S → H → W and, within a given kind of milk concentrates, with temperature increase. It is known that the positive effect

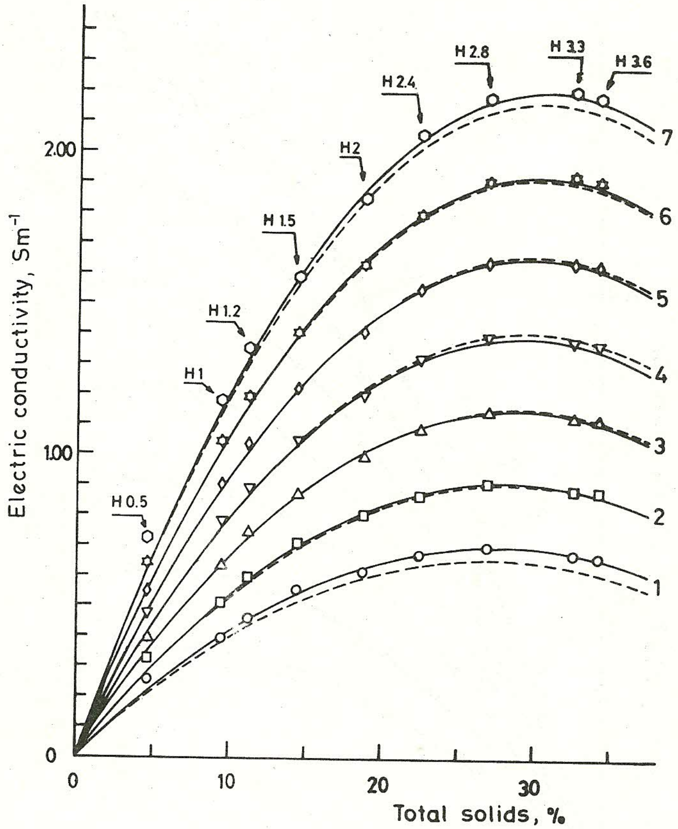

Fig. 5. Effect of concentration on electrical conductivity of half-half milk concentrates. 1: 10 °C; 2: 20 °C; 3: 30 °C; 4: 40 °C; 5: 50 °C; 6: 60 °C; 7: 70 °C

of the increment of the number of ions by concentration becomes counterbalanced and finally exceeded by the appearance of the dissociation regression and by some ionic reduction due to the soluble to colloidal transfer of calcium phosphate. As a general rule, it is also known that temperature positively affects conductivity because of viscosity reduction and increment in ionization degree, moreover, it increases acidity by displacement of the buffer capacity of milk salts but acidity and temperature reduce calcium phosphate solubility. All of these factors, among other minor ones, allow an explanation for the conductivity versus dry matter general behaviour of milk concentrates, but it is also likely that their interactions make it difficult to determine the inversion point of the ascending-descending conductivity profile. This could be particularly true in the case of laboratory preparation of concentrates where sample standardization proved

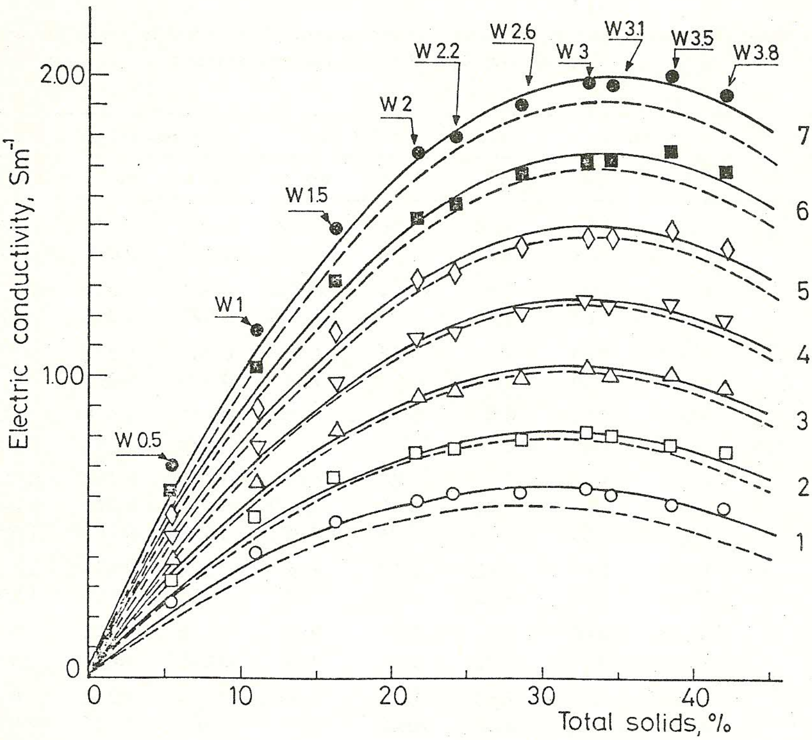

Fig. 6. Effect of concentration on electrical conductivity of whole milk concentrates. 1: 10 °C; 2: 20 °C; 3: 30 °C; 4: 40 °C; 5: 50 °C; 6: 60 °C; 7: 70 °C

rather difficult to achieve. To illustrate how acidity and viscosity may influence conductivity some experimental results at 3 temperatures are given in Table 2 for pairs of samples, very close in composition, corresponding to 8 types of concentrates.

Samples with the higher viscosity were obtained by appropriate dilution with deionized-distilled water of much higher concentrated ones, so that thermal induced effects on serum proteins and calcium phosphate would be expected to be stronger than in those directly concentrated up to the required level. It can be seen that the increase in temperature always enlarged any initial difference in conductivity. Acidity seemed to play a minor role. Viscosity, however, appeared to be the major responsible factor for conductivity variations. In this respect Rogov and Gorbatov [16] reported, for whole milk ranging in composition between 13—11% total solids and 3—6% fat content, the constant value of the product of its electrical conductivity by its viscosity in the temperature range of 50—80 °C. Pino and Chiofalo [14, 15] did not find any relationship between

Table 2

Acidity, viscosity and conductivity at three temperatures on pairs of samples with nearly the same composition, concerning eight different milk concentrates

Sample	Acidity		Viscosity, 10^{-3} X Nsm^{-2}			Conductivity, Sm^{-1}		
	s%	g/l	15 °C	40 °C	60 °C	15 °C	40 °C	60 °C
S1A	8.31	1.37	1.83	1.06	0.760	0.499	0.814	1.093
S1B	8.16	1.38	1.79	1.04	0.757	0.493	0.806	1.082
S1.4A	11.76	1.95	2.14	1.24	0.903	0.631	1.051	1.446
S1.4B	11.42	1.61	2.10	1.20	0.870	0.628	1.043	1.422
S2A	16.09	2.93	3.11	1.66	1.15	0.749	1.265	1.721
S2B	15.59	3.14	2.92	1.64	1.11	0.805	1.367	1.871
S2.9A	23.81	4.77	6.08	2.86	1.90	0.877	1.525	2.111
S2.9B	23.20	4.95	6.23	3.02	1.93	0.940	1.635	2.259
W1A	11.60	1.63	2.71	1.55	1.07	0.440	0.728	0.983
W1B	11.58	1.64	1.91	1.15	0.840	0.479	0.779	1.047
W1C	11.30	1.59	2.33	1.34	0.991	0.453	0.748	1.003
W1.5A	16.67	2.88	4.48	2.32	1.58	0.555	0.934	1.265
W1.5B	16.45	3.14	3.52	1.88	1.35	0.580	0.962	1.299
W2A	21.54	3.46	6.01	2.91	2.05	0.664	1.116	1.519
W2B	21.50	3.36	7.84	3.81	2.50	0.638	1.082	1.474
W2.6A	28.68	4.81	19.88	9.24	5.70	0.705	1.219	1.677
W2.6B	28.38	4.73	19.91	10.00	6.02	0.694	1.204	1.663

both physical properties for mixed milk during transport and refrigerated conservation, while Sudheendranath and Rao [17] reported a correlation for skim-milk only in the case of certain breeds of cows and certain temperatures. Analysis of data from Table 2 led to the expression $\kappa \circ \eta^a = b$ where constants a and b were characteristics, highly significant (***), of each kind of sample. A general expression could then be formulated as a function of the solids content as follows:

$$\kappa \circ \eta^{(1-0.011s)} = 2.038 - 0.230s + 0.0127s^2$$

where κ is given in Sm^{-1}, η in 10^{-3} X Nsm^{-2} and s in %. The equation allows the computation of conductivity when viscosity at a given temperature between 15–60 °C is known for any milk with total solids up to about 30%.

Conductivity prediction

The parameter coefficients of the functions above-mentioned $\kappa = \phi\,(s)$ were first related to temperature within each series of samples in order to find an expression for every S-, H- and W-type of milk concentrates. The three equations were in turn related

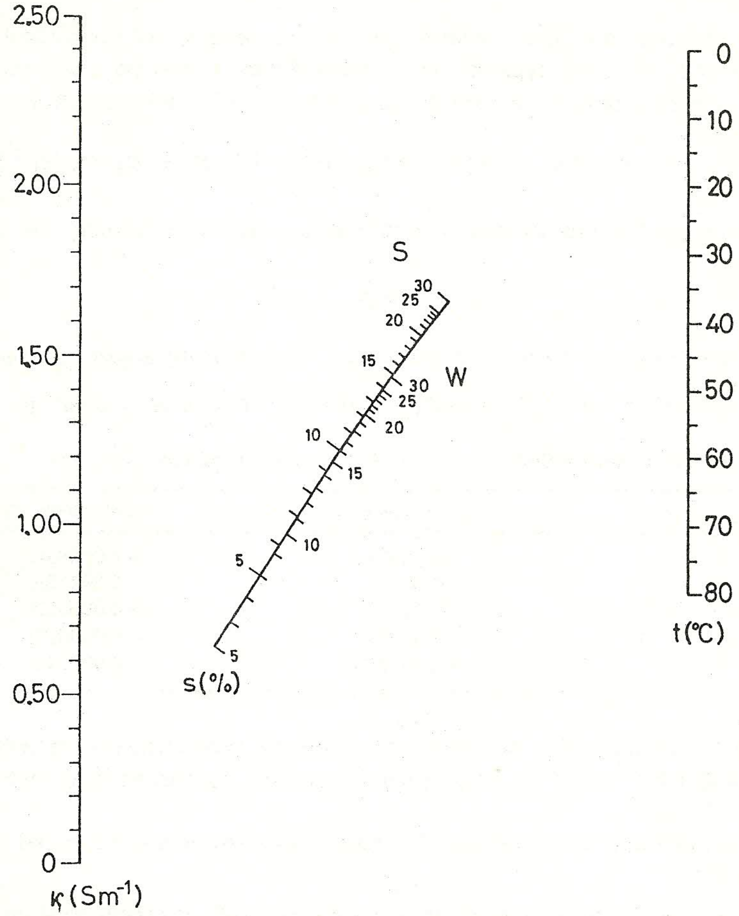

Fig. 7. Nomogram to compute (straight-edge method) electrical conductivity from temperature and solids content in the three kinds of milk concentrates

to one another through the ratio r or fat to solid-nonfat content, a compositional parameter characteristic of each type of milk concentrates. In this way, and within the experimental ranges concerned, a general expression could be formulated as follows:

$$\kappa = \{(B_0 + B_1 r) + (C_0 + C_1 r)s + [(B_2 + C_2 s) + (B_3 + C_3 s)r + (B_4 + C_4 s)r^2]t\}s$$

where parameter coefficients B_i and C_i obtained by regression methods are given in Table 3.

Table 3

Regression values of the parameter coefficients B_i and C_i in the general expression

$$\kappa = \{(B_0 + B_1 r) + (C_0 + C_1 r)s + [(B_2 + C_2 s) + (B_3 + C_3 s)r + (B_4 + C_4 s)r^2]t\}s$$

where κ is given in Sm^{-1}, s in %, t in °C and r is a dimensionless parameter

Serial number	Coefficients B_i	Coefficients C_i
0	0.0399	− 0.000828
1	−0.0443	0.001135
2	0.00179	− 0.0000239
3	−0.000837	− 0.0000325
4	−0.004268	0.000213

Calculated values from this expression fitted all the experimental data with a s.d. $(n = 420) = 0.052$ Sm^{-1}, and are graphically represented by dashed lines in Figs 4, 5 and 6.

In order to facilitate computation, this general expression was converted into the nomogram of Fig. 7.

By means of this N-type nomogram (straight-edge method), electrical conductivity of milk concentrates can be known from temperature and solids content. The scale for half and half milk concentrates was not plotted for the sake of clarity. The pivot point for any given solids content percentage x of H-concentrate can easily be obtained by drawing the middle point on the segment defined by the respective pivot points for the S- and W-concentrates of the same x composition. Application of the nomogram was restricted, by practical reasons, to the region of increasing conductivity. Some precision was thus gained with respect to the analytical solution and the corresponding conductivity estimates could then be made with a lower s.d. (0.038; $n = 345$).

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