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# PHYSICO-CHEMICAL PROPERTIES OF THE SODIUM SALTS OF SOME FATTY ACIDS IN FORMAMIDE SOLUTION IN THE TEMPERATURE RANGE 15—45°C

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In continuation of our earlier work [1] on the determination of the apparent and partial molal volumes of potassium halides in formamide, density measurements of the sodium salts of formic, acetic, propionic, *n*-butyric and *n*-valeric acids in formamide solution have been made at seven different temperatures ranging from 15 to 45°C, and the data analysed on the basis of Masson's equation [2], to determine the effect of the increase in chain length upon the change in apparent and partial molal volumes and expansibilities.

## EXPERIMENTAL

Sodium formate and sodium acetate (B.D.H., L.R.s) were recrystallized three times from conductivity water. Sodium salts of propionic, *n*-butyric and *n*-valeric acids were prepared as described earlier [3]. These salts were dried at 100°C for 2 h and kept in a vacuum desiccator before use. The method of purification of formamide and the procedure of density measurements were essentially similar to that described in our previous article [1].

## RESULTS AND DISCUSSION

As usual [1], the apparent molal volumes, $\phi_v$, calculated from the equation

$$\phi_v = \frac{1000}{cd_0}(d_0 - d) + \frac{M_2}{d_0} \tag{1}$$

where the symbols have their usual significance, were found to vary linearly with $c^{1/2}$ according to Masson's equation. Masson's plots for various sodium salts in formamide at the experimental temperatures were linear, and the values of $\phi_v^0$, the apparent molal volume at infinite dilution, obtained from the extrapolation of the plot of $\phi_v$ vs. $c^{1/2}$ to $c = 0$ are presented in Table 1, along with the limiting slopes, $S_v$, and the increments in $\phi_v^0$ due to an increase in chain length of a $CH_2$ grouping.

TABLE 1

Values of $\phi_v^0$, $S_v$, $A$ and $B$ [eqn. (2)], $\overline{V}_{2\max}$ and $\Delta\phi_v^0$ for sodium formate, acetate, propionate, butyrate and valerate at different temperatures

| Temp. (°C) | Salts [a] | $\phi_v^0$ (ml mole$^{-1}$) | $S_v$ (ml$^{3/2}$ mole$^{-3/2}$) | $A \times 10^2$ | $B \times 10^2$ | $\overline{V}_{2\max}$ (ml mole$^{-1}$) | Mean $\Delta\phi_v^0$ (ml mole$^{-1}$) per $CH_2$ increase |
|---|---|---|---|---|---|---|---|
| 15 | a | 28.48 | 2.99 | 3.5670 | 0.3389 | 32.93 | 16.08 |
| | b | 44.57 | 3.09 | 3.1290 | 0.3322 | 50.27 | |
| | c | 60.59 | 3.42 | 2.7156 | 0.3882 | 66.94 | |
| | d | 76.73 | 3.63 | 2.2822 | 0.4160 | 83.27 | |
| | e | 92.81 | 4.12 | 1.8494 | 0.4665 | 100.26 | |
| 20 | a | 28.82 | 2.95 | 3.5405 | 0.3314 | 34.18 | 16.11 |
| | b | 44.94 | 3.04 | 3.1158 | 0.3446 | 50.54 | |
| | c | 60.98 | 3.37 | 2.6980 | 0.3828 | 67.24 | |
| | d | 77.11 | 3.64 | 2.2665 | 0.4094 | 83.63 | |
| | e | 93.24 | 4.10 | 1.8413 | 0.4656 | 100.64 | |
| 25 | a | 29.17 | 2.88 | 3.5145 | 0.3241 | 34.39 | 16 |
| | b | 45.30 | 2.99 | 3.0949 | 0.3388 | 50.79 | |
| | c | 61.37 | 3.32 | 2.6790 | 0.3755 | 67.53 | |
| | d | 77.55 | 3.56 | 2.2516 | 0.4027 | 83.94 | |
| | e | 93.70 | 4.05 | 1.8288 | 0.4674 | 100.98 | |
| 30 | a | 29.51 | 2.81 | 3.4912 | 0.3195 | 34.62 | 16.17 |
| | b | 45.64 | 2.96 | 3.0733 | 0.3328 | 51.07 | |
| | c | 61.74 | 3.30 | 2.6608 | 0.3696 | 67.85 | |
| | d | 78.02 | 3.47 | 2.2443 | 0.4057 | 84.24 | |
| | e | 94.17 | 3.98 | 1.8180 | 0.4521 | 101.33 | |
| 35 | a | 29.85 | 2.76 | 3.4660 | 0.3129 | 34.84 | 16.19 |
| | b | 46.02 | 2.90 | 3.0532 | 0.3280 | 51.32 | |
| | c | 62.14 | 3.25 | 2.6393 | 0.3601 | 68.13 | |
| | d | 78.38 | 3.50 | 2.2208 | 0.3892 | 84.61 | |
| | e | 94.60 | 3.96 | 1.8033 | 0.4424 | 101.70 | |
| 40 | a | 30.18 | 2.72 | 3.4398 | 0.3053 | 35.09 | 16.22 |
| | b | 46.37 | 2.86 | 3.0342 | 0.3236 | 51.60 | |
| | c | 62.52 | 3.22 | 2.6262 | 0.3592 | 68.44 | |
| | d | 78.81 | 3.44 | 2.2073 | 0.3836 | 84.93 | |
| | e | 95.04 | 3.92 | 1.7935 | 0.4370 | 102.06 | |
| 45 | a | 30.50 | 2.68 | 3.4168 | 0.2987 | 35.32 | 16.25 |
| | b | 46.70 | 2.85 | 3.0129 | 0.3154 | 51.88 | |
| | c | 62.93 | 3.15 | 2.6102 | 0.3514 | 68.72 | |
| | d | 79.25 | 3.36 | 2.1953 | 0.3770 | 85.23 | |
| | e | 95.50 | 3.87 | 1.7851 | 0.4301 | 102.41 | |

[a] a = Sodium formate; b = sodium acetate; c = sodium propionate; d = sodium butyrate; e = sodium valerate.

The densities of the sodium salt solutions in formamide were calculated by the usual relation [1] and have been expressed in the general form

$$d = d_0 + Ac - Bc^{3/2} \qquad (2)$$

which agrees fairly well with the observed density values. The constants $A$

and $B$ of eqn. (2) are also included in Table 1.

As usual, the partial molal volumes, $\overline{V}_2$, were calculated by the relation [4]

$$\overline{V}_2 = \phi_v + \left(\frac{1000 - c\phi_v}{2000 + S_v c^{3/2}}\right) S_v c^{1/2} \tag{3}$$

for the sodium salts at different temperatures for various concentrations of the solutions. The partial molal volumes at the highest concentration, $\overline{V}_{2\max}$, for different temperatures are also presented in Table 1.

The partial molal expansibilities, $\overline{E}_2$, for the sodium salts have been calculated by using the equation [1]

$$\overline{E}_2 = \phi_E + \left(\frac{1000 - c\phi_E}{2000 + S_E c^{3/2}}\right) S_E c^{1/2} \tag{4}$$

where the symbols have their usual meaning. The values of the apparent molal expansibility ($\phi_E$) of the solution were calculated from the equation

$$\phi_E = \alpha_0 \phi_v + (\alpha - \alpha_0)\frac{1000}{c} \tag{5}$$

where $\alpha$ and $\alpha_0$ are the coefficients of thermal expansion of solution and solvent, respectively, as defined earlier, and the values of $\alpha$ and $\phi_E$ can be represented by the expressions of the forms

$$\alpha = \alpha_0 + A'c - B'c^{3/2} \tag{6}$$

and

$$\phi_E = \phi_E^0 + S_E C^{1/2} \tag{7}$$

respectively. The constants for eqns. (6) and (7) are summarized in Table 2 at different temperatures and 1 atm pressure, together with the increments in $\phi_E^0$ due to an increase in chain length of a $CH_2$ grouping.

The fact that the apparent molal volumes of the sodium salts of fatty acids increase with increase of concentration is in agreement with our earlier observations on potassium halides in formamide. Comparing the present set of data with that available in aqueous medium [5] it is seen that the limiting apparent molal volumes, $\phi_v^0$ and the slopes, $S_v$ are more in formamide than in aqueous medium. As usual, the more positive values of $S_v$ in formamide indicate the greater electrostatic ion—ion interaction in this solvent than in water. As apparent in Table 1, the $S_v$ values at a particular temperature are increasingly positive as the chain length of a $CH_2$ grouping increases but decrease slightly with the rise in temperature. A similar trend is also observed in aqueous medium.

The limiting apparent molal volume, $\phi_v^0$ of sodium salts of fatty acids like in aqueous medium [5] increases with increase of temperature and has been given in the form

$$\phi_v^0 = C + DT \tag{8}$$

showing the variation of $\phi_v^0$ with any temperature $T$ (in °C). As expected, the limiting apparent molal volume is found to increase with increase in chain

TABLE 2

Values of $\phi_E^0$, $S_E$, $A'$ and $B'$ [eqn. (6)] and $\Delta\phi_E^0$ for sodium formate, acetate, propionate, butyrate and valerate at different temperatures and one atmospheric pressure

| Temp. (°C) | Salts [a] | $\phi_E^0 \times 10^2$ (ml mole$^{-1}$) | $-S_E \times 10^2$ (ml$^{3/2}$ mole$^{-3/2}$) | $A' \times 10^4$ | $B' \times 10^4$ | Mean $\Delta\phi_E^0 \times 10^2$ (ml mole$^{-1}$) per $CH_2$ increase |
|---|---|---|---|---|---|---|
| 15 | a | 6.14 | 0.79 | 0.405 | 0.101 | 0.623 |
| | b | 6.86 | 0.92 | 0.359 | 0.114 | |
| | c | 7.42 | 0.83 | 0.316 | 0.108 | |
| | d | 8.14 | 0.97 | 0.250 | 0.123 | |
| | e | 8.70 | 0.90 | 0.189 | 0.120 | |
| 20 | a | 6.21 | 0.81 | 0.409 | 0.102 | 0.638 |
| | b | 6.94 | 0.92 | 0.361 | 0.114 | |
| | c | 7.45 | 0.79 | 0.300 | 0.110 | |
| | d | 8.22 | 0.99 | 0.254 | 0.125 | |
| | e | 8.76 | 0.89 | 0.190 | 0.120 | |
| 25 | a | 6.30 | 0.83 | 0.414 | 0.104 | 0.640 |
| | b | 7.02 | 0.93 | 0.367 | 0.116 | |
| | c | 7.60 | 0.88 | 0.307 | 0.113 | |
| | d | 8.33 | 1.03 | 0.259 | 0.129 | |
| | e | 8.79 | 0.85 | 0.195 | 0.125 | |
| 30 | a | 6.39 | 0.85 | 0.420 | 0.106 | 0.643 |
| | b | 7.10 | 0.95 | 0.371 | 0.117 | |
| | c | 7.71 | 0.72 | 0.311 | 0.115 | |
| | d | 8.41 | 1.05 | 0.262 | 0.130 | |
| | e | 8.96 | 0.96 | 0.197 | 0.126 | |
| 35 | a | 6.46 | 0.86 | 0.425 | 0.107 | 0.648 |
| | b | 7.17 | 0.96 | 0.374 | 0.118 | |
| | c | 7.78 | 0.93 | 0.316 | 0.118 | |
| | d | 8.48 | 1.05 | 0.264 | 0.131 | |
| | e | 9.05 | 0.99 | 0.198 | 0.127 | |
| 40 | a | 6.54 | 0.87 | 0.430 | 0.108 | 0.648 |
| | b | 7.26 | 0.99 | 0.379 | 0.119 | |
| | c | 7.86 | 0.95 | 0.318 | 0.118 | |
| | d | 8.57 | 1.08 | 0.269 | 0.134 | |
| | e | 9.13 | 1.01 | 0.201 | 0.130 | |
| 45 | a | 6.62 | 0.89 | 0.433 | 0.109 | 0.643 |
| | b | 7.32 | 0.98 | 0.381 | 0.119 | |
| | c | 7.92 | 0.95 | 0.319 | 0.118 | |
| | d | 8.63 | 1.09 | 0.268 | 0.133 | |
| | e | 9.19 | 1.01 | 0.202 | 0.130 | |

[a] a = Sodium formate; b = sodium acetate; c = sodium propionate; d = sodium butyrate; e = sodium valerate.

length of a $CH_2$ grouping corresponding to the magnitude of increase in ion—ion interaction in this solvent.

The limiting apparent molal expansibility, $\phi_E^0$ of these sodium salts as obtained in the present study is found to follow a similar trend to that of $\phi_V^0$ in

TABLE 3

Parameters for eqns. (8) and (9)

| Salts | $C$ | $D$ | $C' \times 10^2$ | $D' \times 10^2$ |
|---|---|---|---|---|
| Formate | 27.474 | 0.068 | 5.50 | 0.030 |
| Acetate | 43.521 | 0.071 | 6.63 | 0.016 |
| Propionate | 59.424 | 0.078 | 7.14 | 0.018 |
| *n*-Butyrate | 75.452 | 0.084 | 7.95 | 0.015 |
| *n*-Valerate | 91.458 | 0.090 | 8.41 | 0.018 |

this solvent and has been expressed as a function of temperature by the equation of the form

$$\phi_E^0 = C' + D'T \qquad (9)$$

The constants for eqns. (8) and (9) by means of which the limiting apparent molal volume and expansibility may be calculated are presented in Table 3 for different sodium salts. Also, the limiting apparent molal expansibility is found to increase with increase in chain length, indicating the decreasing tendency of ion—solvent interaction and solvation as the chain length of a $CH_2$ grouping increases.

The partial molal volumes, $\overline{V}_2$ for the sodium salts increase with increase in concentration tending to a constant value for each temperature, agreeing fairly well with our earlier observation on the potassium halides in formamide. In Table 1 the partial molal volumes at the highest concentration, $\overline{V}_{2\max}$, are reported for the sodium salts at different temperatures. As observed, $\overline{V}_{2\max}$ increases with increase in chain length of a $CH_2$ grouping owing to the structure-breaking of the solvent molecules in concentrated solutions of anions of bigger size.

The $\Delta\phi_v^0$ values listed in Table 1 show a value of approximately 16.13 ml per $CH_2$ increase at infinite dilution, increasing slightly with increasing concentration. This mean value of 16.13 ml is somewhat more than the value of 14.6 ml used by Watson and Felsing [5] at 0.5—3.0 molal aqueous solutions of sodium salts of fatty acids but is in good agreement with 16.3 ml used by Cohn et al. [6] for the $CH_2$ increase of certain aliphatic and amino acids at 0.25 molal aqueous solutions. The higher $\Delta\phi_v^0$ value in formamide might be due to the greater structure-breaking effect of the sodium salts in formamide than in water.

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