

THE TEMPERATURE DEPENDENCE OF INTERMOLECULAR ACTIVATION ENERGY FOR FLOW IN LIQUID AND SOLUTIONS

Part VIII.—Influence of Sodium Chloride Concentration on the Activation Energy Jumps Observed in Water

A.K.M. AHSANULLAH, MOHD. ESHAQUE MIAN and M.M. QURASHI*

P.C.S.I.R. Laboratories, Karachi 32

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Accurate measurements of flow activation energy of aqueous sodium chloride solutions (0 to 2% by weight) at close intervals of concentration (in the temperature range of 10° to 50°C) have been undertaken and reported in this communication. On examining the results for the temperature of the jumps observed in $10^{-3}E_{\eta}/R$, and the "supercooling" effect persisting in these NaCl solutions, one may infer that cooperative structural breaking up and reforming occurs within the various sodium chloride solutions, but certain concentrations of NaCl strongly modify the water structure persisting in all these solutions. This may lead to appearance, disappearance, and coalescence of certain steps (as experimentally observed in these solutions) with change in magnitude of the jumps, through either volume or surface-induced ordering in a thin layer.

1. Introduction

In an earlier communication,¹ some measurements were presented on the temperature variation of flow activation energy of aqueous sodium chloride (0 to 1%), in the temperature range from 15°C to 50°C, and a series of well-defined jumps like those of pure water² were observed. It was also noticed that the plots of values of $10^{-3} \times E/R$ (reproduced in Fig. 1) for the cooling sequences were strikingly different from corresponding plots for heating sequence. This is in agreement with earlier findings with solutions containing 20% and 30% by weight ethanol,³ and indicates the possible existence of a phenomenon akin to supercooling. The amplitude of this supercooling type of variation showed a tendency to increase as the concentration increases, and could ultimately give a clear oscillatory behaviour, as found with concentrated solutions^{4,5} of $\text{Sr}(\text{NO}_3)_2$, NH_4NO_3 and KCl . This may be a significant point. In order to examine this, and further to investigate the influence of sodium chloride concentration on the temperature of the activation energy jumps already observed in water,² several measurements on intermediate concentrations as well as higher concentrations of sodium chloride (0 to 2%) were undertaken, and are reported here.

2. Experimental Technique

The measuring technique is the same as adopted earlier for water² and dilute alcohol,³ being based on the differential of the logarithm of the Andrade equation, viz.

$$\begin{aligned} (E_{\eta}/R) &= \Delta \ln \eta / \Delta (1/T) = -T^2 \Delta \ln \eta / \Delta T \dots \dots (1) \\ &= (-T^2 \Delta \ln \nu / \Delta T + T^2 \beta = E_{\nu}/R + T^2 \beta, \text{ where } T^2 \beta \\ &= T^2 (\Delta \rho / \Delta T)_{\rho} \text{ is a small correction term involv-} \end{aligned}$$

*Now at P.C.S.I.R. Laboratories, Peshawar.

ing β , the coefficient of dilatation of the experimental sample. The apparatus used in these experiments is the same as that for previously reported measurements on water,² including the vapour-equilibrium bottle containing a relatively large surface of the particular solution under

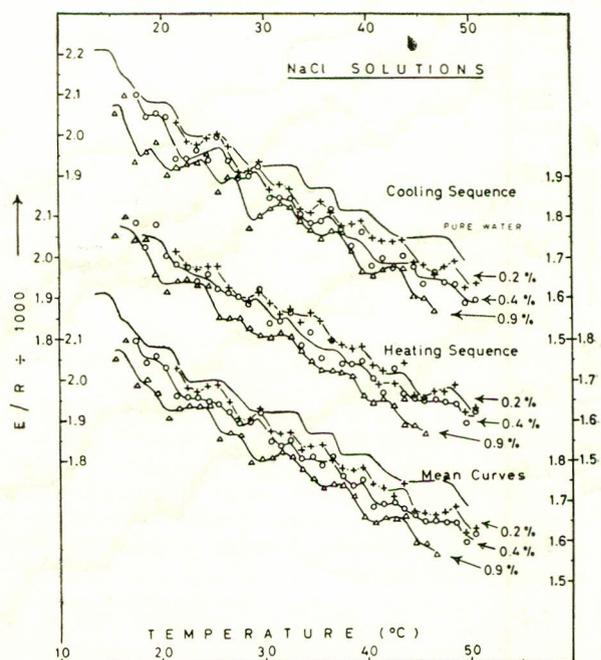


Fig. 1.—Reproduction of graphs of $E/R \div 1000$ in the range of 15°C to 50°C for 0.2, 0.4 and 0.9% aqueous NaCl (by weight) from an earlier paper. The upper curves are for the cooling sequences, the middle three for the heating sequences, while the lowest three are the means for each solution. The stepwise character is seen in heating sequences, while the supercooling type of phenomena are observed in the cooling sequences.

test. The measurements of flow times are made with B.S.S. U-tube viscometer No. 1, at intervals of 1 degree C, by using a calibrated Beckmann differential thermometer, the temperature during each flow time measurement being maintained to within $\pm 0.002^\circ\text{C}$.

3. Experimental results for 1.2, 1.6 and 2% Sodium Chloride in Water

Extra pure, crystalline sodium chloride (E. Merck, Germany) was used for the various solutions, which were prepared by adding a measured quantity of pure sodium chloride to triple-distilled water in a stoppered flask and shaking thoroughly. The sodium chloride percentages were then checked by (i) density measurement, and (ii) viscosity measurement at a suitable temperature in the course of the main experiment.

During the earlier series of experiments, (Fig. 1) it was noticed that the value of $10^{-3} \times E\eta/R$ for sodium chloride solutions (0.2, 0.4 and 0.9%) were decreasing gradually with the increase of concentration from 0 to 1%. It was, therefore, thought best to first make a series of measurements for 1 to 2% sodium chloride at intervals of 0.4%, and therefore new measurements have been made on 1.2, 1.6 and 2% aqueous sodium chloride. The experimental data for 1.2% sodium chloride solution with heating and cooling sequences are shown in Table 1(a), together with the standard deviations as estimated from (i) the scatter of repeated observations of flow times and temperature and (ii) the differences between the values of $E\eta/R$ with heating and cooling sequences. Table 1(b) and (c) gives the overall mean values of $10^{-3} \times E\eta/R$ for 1.6 and 2% solutions, which are plotted as hollow circles in Fig. 2, where the top

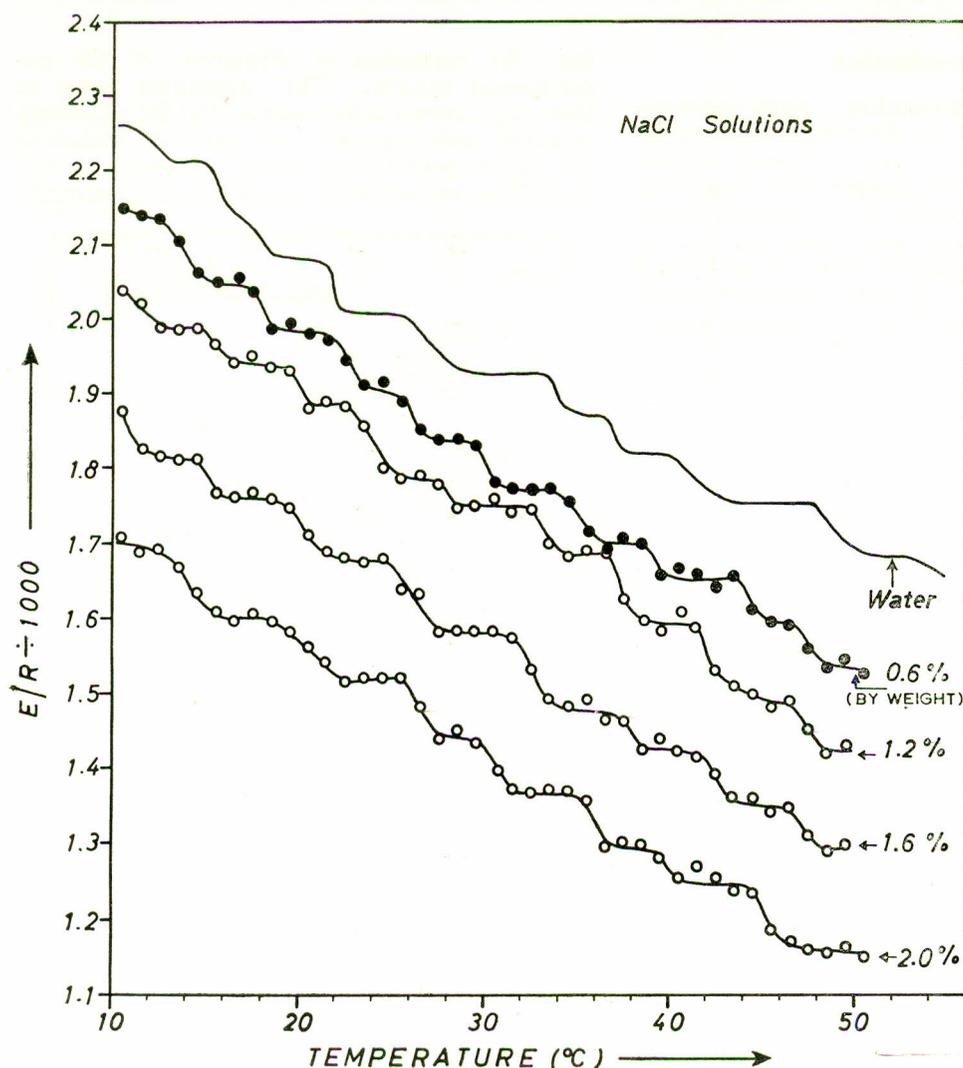


Fig. 2.—Mean $E/R \div 1000$ values against temperature from 10°C to 50°C for four percentages of NaCl (0.6, 1.2, 1.6 and 2% by weight). It is seen that, by and large, the presence of energy levels persists in these solutions of NaCl, and as the concentration of NaCl increases, the amplitude of variation also increases, with a corresponding increase in the depth of the jumps.

full-line curve is for pure water. The graph for each solution is shifted 0.1 unit downwards from the full-line curve. The average standard deviation for 1.2% solutions is of the order of 0.007, and the differences between the heating and cooling sequence values are in general higher than this

standard deviation. Accordingly, Table 1(a) also gives the deviation of the cooling and the heating sequence values from their overall mean (the upper sign being for cooling sequence values), together with the r.m.s. values of these deviations calculated for groups of ten temperatures as shown

TABLE 1(a).—EXPERIMENTAL VALUES OF $(E/R) \div 1000 = -T^2 (\Delta \ln v / \Delta T) / 1000$ FOR 1.2% SODIUM CHLORIDE SOLUTION

Temp. (°C)	$(E/R) \div 1000 = -T^2 (\Delta \ln v / \Delta T) / 1000$			Standard deviations for the group of ten.
	Heating sequence	Cooling sequence	Mean $(E/R) \div 1000$	
10.50	2.255 ± 0.009	2.225 ± 0.004	2.240 ± 0.015	0.007 and 0.017
11.50	2.173 ± 0.009	2.271 ± 0.004	2.222 ± 0.049	
12.50	2.165 ± 0.009	2.215 ± 0.004	2.190 ± 0.025	
13.50	2.190 ± 0.009	2.180 ± 0.004	2.185 ± 0.005	
14.50	2.201 ± 0.009	2.175 ± 0.004	2.188 ± 0.013	
15.50	2.180 ± 0.007	2.156 ± 0.006	2.168 ± 0.012	
16.50	2.136 ± 0.007	2.144 ± 0.006	2.140 ± 0.004	
17.50	2.130 ± 0.007	2.174 ± 0.006	2.152 ± 0.022	
18.50	2.133 ± 0.007	2.137 ± 0.006	2.135 ± 0.002	
19.50	2.133 ± 0.007	2.127 ± 0.006	2.130 ± 0.003	
20.50	2.066 ± 0.007	2.092 ± 0.004	2.079 ± 0.013	0.008 and 0.020
21.50	2.095 ± 0.007	2.083 ± 0.004	2.089 ± 0.006	
22.50	2.116 ± 0.007	2.052 ± 0.004	2.084 ± 0.032	
23.50	2.029 ± 0.007	2.081 ± 0.004	2.055 ± 0.026	
24.50	1.990 ± 0.007	2.006 ± 0.004	1.998 ± 0.008	
25.50	2.013 ± 0.006	1.959 ± 0.010	1.986 ± 0.027	
26.50	1.980 ± 0.006	2.004 ± 0.010	1.992 ± 0.012	
27.50	1.997 ± 0.006	1.957 ± 0.010	1.977 ± 0.020	
28.50	1.931 ± 0.006	1.959 ± 0.010	1.945 ± 0.014	
29.50	1.954 ± 0.006	1.946 ± 0.010	1.950 ± 0.004	
30.50	1.967 ± 0.004	1.951 ± 0.002	1.959 ± 0.008	0.004 and 0.019
31.50	1.897 ± 0.004	1.985 ± 0.002	1.941 ± 0.044	
32.50	1.897 ± 0.004	1.992 ± 0.002	1.945 ± 0.047	
33.50	1.909 ± 0.004	1.887 ± 0.002	1.898 ± 0.011	
34.50	1.887 ± 0.004	1.873 ± 0.002	1.880 ± 0.007	
35.50	1.886 ± 0.004	1.894 ± 0.004	1.890 ± 0.004	
36.50	1.888 ± 0.004	1.884 ± 0.004	1.886 ± 0.002	
37.50	1.829 ± 0.004	1.821 ± 0.004	1.825 ± 0.004	
38.50	1.785 ± 0.004	1.807 ± 0.004	1.796 ± 0.011	
39.50	1.795 ± 0.004	1.761 ± 0.004	1.778 ± 0.017	
40.50	1.798 ± 0.004	1.818 ± 0.004	1.808 ± 0.010	0.004 and 0.012
41.50	1.780 ± 0.004	1.789 ± 0.004	1.784 ± 0.005	
42.50	1.733 ± 0.004	1.723 ± 0.004	1.728 ± 0.005	
43.50	1.700 ± 0.004	1.716 ± 0.004	1.708 ± 0.008	
44.50	1.704 ± 0.004	1.692 ± 0.004	1.698 ± 0.006	
45.50	1.682 ± 0.003	1.678 ± 0.003	1.680 ± 0.002	
46.50	1.704 ± 0.003	1.674 ± 0.003	1.689 ± 0.015	
47.50	1.634 ± 0.003	1.666 ± 0.003	1.650 ± 0.016	
48.50	1.624 ± 0.003	1.610 ± 0.003	1.617 ± 0.007	
49.50	1.649 ± 0.003	1.607 ± 0.003	1.628 ± 0.021	

Mean standard deviation = 0.007 and 0.017

352

A.K.M. AHSANULLAH, M. ESHAQUE and M.M. QURASHI

TABLE I (b).—MEASURED FLOW ACTIVATION ENERGY FOR 1.6% AQUEOUS SODIUM CHLORIDE SOLUTION IN THE RANGE 10° TO 50°C.

Temperature (°C)	10.50	11.50	12.50	13.50	14.50	15.50	16.50	17.50	18.50	19.50	Standard deviation for group of ten
(E/R) ÷ 1000	2.173 ±0.010	2.123 ±0.089	2.115 ±0.037	2.110 ±0.022	2.110 ±0.004	2.069 ±0.026	2.061 ±0.010	2.061 ±0.006	2.059 ±0.019	2.047 ±0.035	0.031
Temperature (°C)	20.50	21.50	22.50	23.50	24.50	25.50	26.50	27.50	28.50	29.50	
(E/R) ÷ 1000	2.008 ±0.050	1.986 ±0.043	1.979 ±0.023	1.972 ±0.001	1.975 ±0.023	1.939 ±0.036	1.932 ±0.005	1.879 ±0.069	1.883 ±0.022	1.882 ±0.048	0.038
Temperature (°C)	30.50	31.50	32.50	33.50	34.50	35.50	36.50	37.50	38.50	39.50	
(E/R) ÷ 1000	1.882 ±0.027	1.874 ±0.005	1.828 ±0.046	1.794 ±0.097	1.779 ±0.038	1.787 ±0.017	1.762 ±0.018	1.761 ±0.024	1.722 ±0.032	1.737 ±0.015	0.038
Temperature (°C)	40.50	41.50	42.50	43.50	44.50	45.50	46.50	47.50	48.50	49.50	
(E/R) ÷ 1000	1.720 ±0.026	1.713 ±0.035	1.690 ±0.052	1.657 ±0.018	1.658 ±0.001	1.637 ±0.025	1.644 ±0.016	1.609 ±0.028	1.589 ±0.007	1.598 ±0.025	0.028

TABLE I (c).—MEASURED FLOW ACTIVATION ENERGY FOR 2.0% SODIUM CHLORIDE IN WATER.

Temperature (°C)	10.50	11.50	12.50	13.50	14.50	15.50	16.50	17.50	18.50	19.50	Standard deviation for group of ten
(E/R) ÷ 1000	2.109 ±0.014	2.087 ±0.001	2.092 ±0.011	2.069 ±0.007	2.034 ±0.004	2.007 ±0.005	1.996 ±0.003	2.006 ±0.004	1.998 ±0.005	1.982 ±0.006	0.007
Temperature (°C)	20.50	21.50	22.50	23.50	24.50	25.50	26.50	27.50	28.50	29.50	
(E/R) ÷ 1000	1.961 ±0.014	1.941 ±0.031	1.913 ±0.008	1.918 ±0.034	1.919 ±0.051	1.819 ±0.007	1.879 ±0.031	1.837 ±0.014	1.849 ±0.006	1.832 ±0.017	0.025
Temperature (°C)	30.47	31.50	32.50	33.50	34.50	35.50	36.50	37.50	38.50	39.50	
(E/R) ÷ 1000	1.794 ±0.034	1.769 ±0.033	1.765 ±0.027	1.768 ±0.015	1.768 ±0.001	1.753 ±0.003	1.693 ±0.003	1.700 ±0.003	1.696 ±0.001	1.681 ±0.024	0.016
Temperature (°C)	40.50	41.50	42.50	43.50	44.50	45.50	46.50	47.50	48.50	49.50	
(E/R) ÷ 1000	1.653 ±0.011	1.668 ±0.013	1.653 ±0.011	1.636 ±0.023	1.633 ±0.033	1.585 ±0.030	1.570 ±0.005	1.558 ±0.006	1.555 ±0.005	1.564 ±0.000	0.012 ±0.001
											Overall mean S.D. 0.024

in the last column. It is seen from the mean graphs of Fig. 2, that, by and large, the presence of energy levels persists in these solutions of NaCl. The average depth of the jumps for 1.2% sodium chloride solution is of the order of 0.060 with an average period of 4.5°C, whereas the period for 1.6% and 2% solutions is 5.0°C and 5.7°C, respectively, with a corresponding increase in the depth of the jump. We may conjecture that this increase in the amplitude of variation is due to the disappearance of certain substeps, which were previously found in the lower concentrations. The movement of some of the main steps can be readily traced in Fig. 2 from pure water through 1.2, 1.6 and 2% sodium chloride.

4. Results with Closer Concentration Intervals from 0 to 1%, and the Concentration-Temperature Chart.

In order to examine the magnitude and nature of the changes taking place in these jumps or steps as the sodium chloride concentration is increased, and to trace out the precise movements of the energy jumps over the gap between the previously reported data for solutions of 0.4 and 0.9%, it is desirable to interpolate measurements with another concentration. Accordingly 0.6% aqueous sodium chloride was prepared and used for the viscosity measurements, with a thermal interval of 1°C and usual precautions, particularly

against the evaporation of the test liquid. The values of $10^{-3} \times E_{\eta}/R$ and the standard deviation calculated from the difference of heating and cooling sequence values are shown in Table 2. The mean values of $10^{-3} \times E_{\eta}/R$ are plotted in Fig. 2 as solid circles, and the graph drawn through

TABLE 2.—EXPERIMENTAL VALUES OF $(E/R) \div 1000 = -T^2 (\Delta \ln \nu / \Delta T) / 1000$ FOR 0.6% AQUEOUS SODIUM CHLORIDE SOLUTION

Temp. (°C)	$(E/R) \div 1000 = -T^2 (\Delta \ln \nu / \Delta T) / 1000$			Standard deviation for the group of ten
	Heating sequence	Cooling sequence	Mean $(E/R) \div 1000$	
10.50	2.267 ± 0.007	2.231 ± 0.008	2.249 ± 0.018	
11.50	2.242 ± 0.007	2.234 ± 0.008	2.238 ± 0.004	
12.50	2.229 ± 0.007	2.239 ± 0.008	2.234 ± 0.005	
13.50	2.200 ± 0.007	2.208 ± 0.008	2.204 ± 0.004	
14.50	2.172 ± 0.007	2.154 ± 0.008	2.163 ± 0.009	0.009
15.50	2.154 ± 0.006	2.146 ± 0.009	2.150 ± 0.004	
16.50	2.154 ± 0.006	2.158 ± 0.009	2.156 ± 0.002	
17.50	2.126 ± 0.006	2.142 ± 0.009	2.134 ± 0.008	
18.50	2.090 ± 0.006	2.080 ± 0.009	2.085 ± 0.005	
19.50	2.106 ± 0.006	2.082 ± 0.009	2.094 ± 0.012	
20.50	2.086 ± 0.007	2.074 ± 0.010	2.080 ± 0.006	
21.50	2.059 ± 0.007	2.085 ± 0.010	2.072 ± 0.013	
22.50	2.050 ± 0.007	2.036 ± 0.010	2.043 ± 0.007	
23.50	2.038 ± 0.007	1.978 ± 0.010	2.008 ± 0.030	
24.50	2.056 ± 0.006	1.970 ± 0.009	2.013 ± 0.043	0.023
25.50	2.020 ± 0.006	1.955 ± 0.009	1.987 ± 0.032	
26.50	1.975 ± 0.006	1.925 ± 0.009	1.950 ± 0.025	
27.50	1.918 ± 0.006	1.955 ± 0.009	1.936 ± 0.019	
28.50	1.932 ± 0.008	1.942 ± 0.007	1.937 ± 0.005	
29.50	1.920 ± 0.008	1.940 ± 0.007	1.930 ± 0.010	
30.50	1.899 ± 0.008	1.862 ± 0.007	1.880 ± 0.018	
31.50	1.897 ± 0.008	1.847 ± 0.007	1.872 ± 0.025	
32.50	1.885 ± 0.008	1.854 ± 0.007	1.869 ± 0.015	
33.50	1.864 ± 0.010	1.880 ± 0.005	1.872 ± 0.008	
34.50	1.876 ± 0.010	1.832 ± 0.005	1.854 ± 0.022	0.018
35.50	1.828 ± 0.010	1.800 ± 0.005	1.814 ± 0.014	
36.50	1.794 ± 0.010	1.787 ± 0.005	1.790 ± 0.003	
37.50	1.788 ± 0.010	1.822 ± 0.005	1.805 ± 0.017	
38.50	1.796 ± 0.005	1.798 ± 0.006	1.797 ± 0.001	
39.50	1.784 ± 0.005	1.727 ± 0.006	1.755 ± 0.028	
40.50	1.772 ± 0.005	1.758 ± 0.006	1.765 ± 0.007	
41.50	1.760 ± 0.005	1.758 ± 0.006	1.759 ± 0.001	
42.50	1.749 ± 0.005	1.729 ± 0.006	1.739 ± 0.010	
43.50	1.761 ± 0.009	1.751 ± 0.008	1.756 ± 0.005	0.008
44.50	1.689 ± 0.009	1.736 ± 0.008	1.712 ± 0.024	
45.50	1.689 ± 0.009	1.699 ± 0.008	1.694 ± 0.005	
46.50	1.695 ± 0.009	1.685 ± 0.008	1.690 ± 0.005	
47.50	1.661 ± 0.009	1.655 ± 0.008	1.658 ± 0.003	
48.50	1.630 ± 0.006	1.638 ± 0.009	1.634 ± 0.004	
49.50	1.648 ± 0.006	1.644 ± 0.009	1.646 ± 0.002	
50.50	1.627 ± 0.006	1.624 ± 0.009	1.625 ± 0.001	
				Overall standard deviation = 0.015.

them again shows a series of flats and jumps in a sequence closely following that observed with pure water.

It is clearly observed in the mean graphs of Fig. 2 that the activation energy of viscous flow of aqueous sodium chloride solutions (0 to 2%) exhibits a series of energy levels in the temperature range studied, which closely resemble those previously observed in pure water. For understanding the exact course of the movements of

activation energy transition as a function of concentration, a synopsis in respect of temperatures at the various energy jumps or transitions, and their depth in terms of $10^{-3} \times E_{\eta}/R$ is given in Table 3. This covers the range of 0 to 2% sodium chloride. The data for 0.2, 0.4 and 0.9% are taken from previously reported data.¹ The various jumps are classified as "large," "medium" or "small", using the mean value of $(E_{\eta}/R) \div 1000 = 0.060$, and we plot the temperature at the jumps for these solutions versus concentra-

TABLE 3.—COMPARISON OF THE OBSERVED TEMPERATURES ($^{\circ}\text{C}$) FOR THE JUMPS IN $(E/R) \div 1000$ AND THE MAGNITUDE OF THE JUMPS FOR VARIOUS AQUEOUS NaCl SOLUTIONS FROM 0% TO 2%.

Concentration of NaCl in water (by wt)														
0%	Temp. $^{\circ}\text{C}$ of jumps	12.4	15.5	17.5	—	22.0	27.4	—	33.8	37.1	41.6	—	49.0	
	Depth of jumps in $10^{-3}E/R$	0.04	0.07	0.06		0.09	0.07		0.06	0.06	0.06		0.08	
0.2%	Temp. $^{\circ}\text{C}$ of jumps	—	—	—	—	21.0	26.2	30.1	33.0	36.2	40.0	43.8	48.9	
	Depth of jumps in $10^{-3}E/R$					0.08	0.09	0.04	0.03	0.06	0.05	0.06	0.06	
0.4%	Temp. $^{\circ}\text{C}$ of jumps	—	—	17.5	—	20.8	26.1	30.0	33.1	37.0	39.9	43.0	49.0	
	Depth of jumps in $10^{-3}E/R$			0.05		0.10	0.05	0.06	0.04	0.06	0.05	0.03	0.05	
0.6%	Temp. $^{\circ}\text{C}$ of jumps	—	13.4	17.9	—	22.4	26.1	30.1	34.6	—	39.0	44.0	47.2	
	Depth of jumps in $10^{-3}E/R$		0.08	0.05		0.08	0.05	0.06	0.07		0.05	0.05	0.05	
0.9%	Temp. $^{\circ}\text{C}$ of jumps	—	—	17.0	19.4	24.9	28.1	—	33.3	—	38.5	43.8	—	
	Depth of jumps in $10^{-3}E/R$			0.05	0.04	0.07	0.05		0.07		0.09	0.05		
1.2%	Temp. $^{\circ}\text{C}$ of jumps	11.01	15.1	—	19.8	23.2	27.8	—	32.6	—	36.7	41.8	47.0	
	Depth of jumps in $10^{-3}E/R$	0.05	0.04		0.05	0.10	0.03		0.07		0.08	0.07	0.06	
1.6%	Temp. $^{\circ}\text{C}$ of jumps	10.4	14.9	—	19.8	—	25.3	—	32.0	—	38.0	42.4	46.8	
	Depth of jumps in $10^{-3}E/R$	0.06	0.05		0.07		0.09		0.09		0.04	0.06	0.05	
2%	Temp. $^{\circ}\text{C}$ of jumps	—	13.6	—	19.4	—	26.0	30.2	—	35.6	39.6	44.8	—	
	Depth of jumps in $10^{-3}E/R$		0.08		0.08		0.07	0.06		0.06	0.04	0.08		

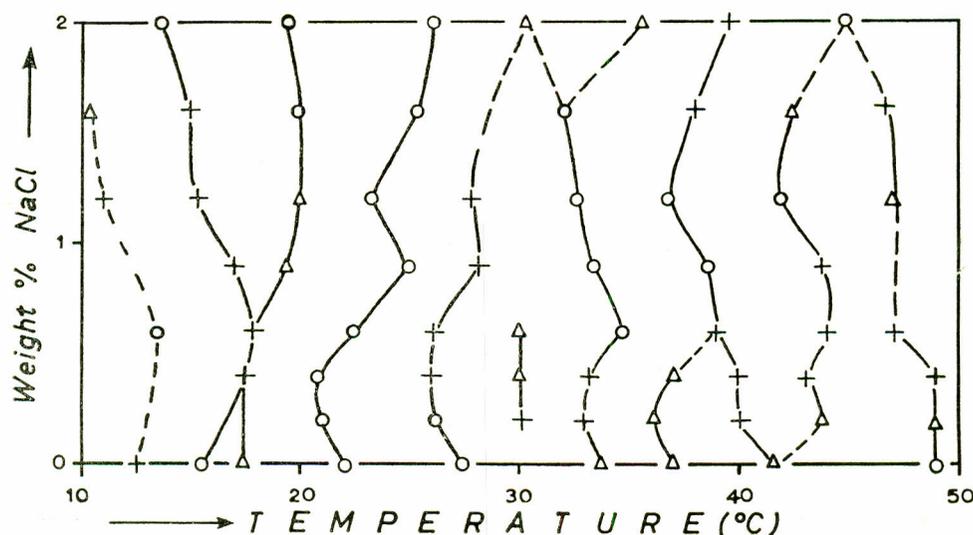


Fig. 3.—Chart showing the temperature of the jumps in the flow activation energy for several NaCl concentrations in the range of 0 to 2% NaCl. The various jumps are classified as large, medium or small (compared with mean values of $(E/R)/1000 = 0.06$), and plotted as circles, triangles and crosses respectively. The full lines connecting several of the plotted points indicate the definite movements of these jumps, while the broken lines stand for those parts involving some ambiguity.

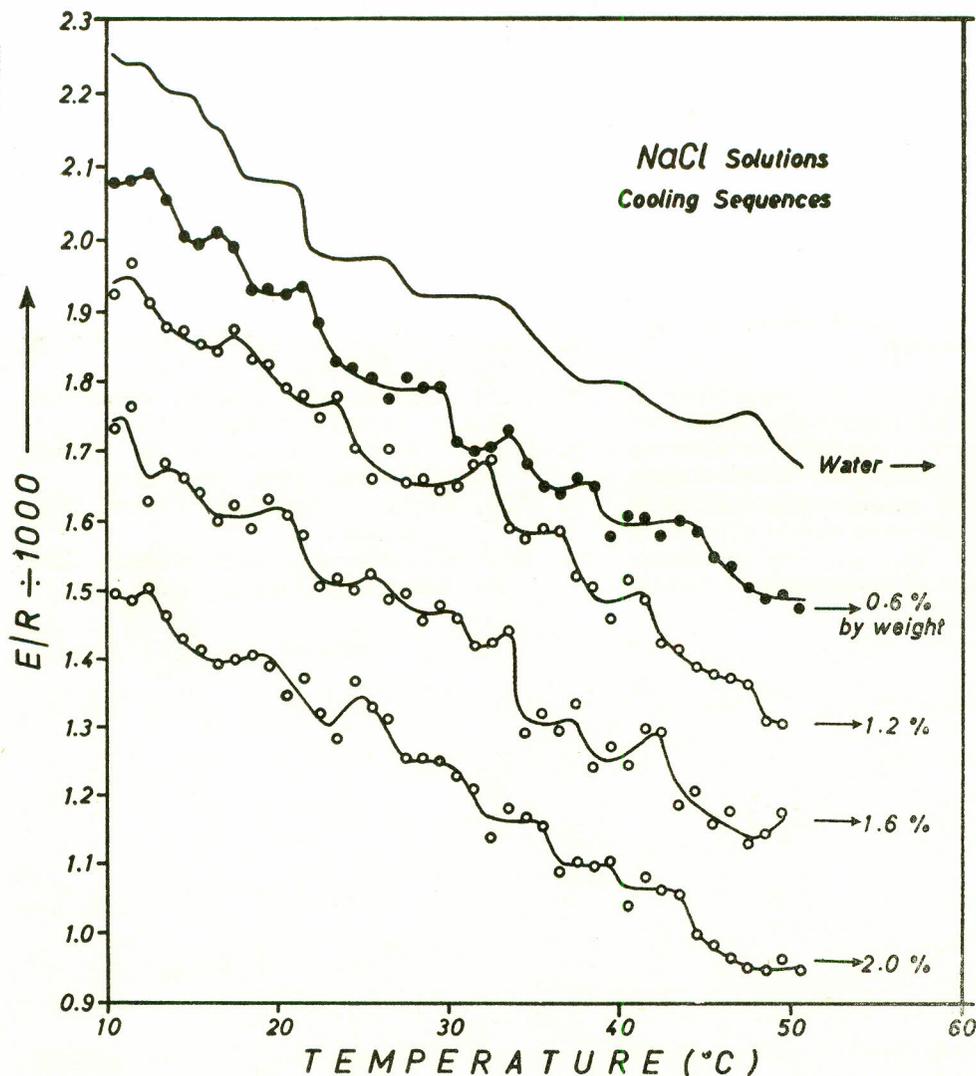


Fig. 4.—Separate plot of cooling sequence values of $10^{-3} E/R$ for 0.6, 1.2, 1.6 and 2% sodium chloride, together with the cooling sequence values of pure water (upper solid line curve). It is seen that no supercooling type of effect is observed in the case of pure water, while such type of effect is exhibited by all these solutions.

tion in Fig. 3, where circles stand for large jumps, triangles for medium, and crosses for small ones. The graphs of Fig. 3 show that most of the plotted points are readily linked together by the full lines, while the points joined by broken lines involve some ambiguity. An examination of this plot shows that while the shift of these jumps with change in concentration is mostly uniform in character, it does not always follow this pattern in some regions, where there is appearance and disappearance of certain steps accompanied by change in magnitude of the jump, in agreement with the earlier findings. Another interesting observation noted from this plot is that the two jumps in pure water at 15.5°C and 17.5°C coalesce at 17.5°C for 0.4% sodium chloride, and separate out again at 17.9°C for 0.6% sodium chloride, while the jumps in water at 37.1°C

and 41.6°C coalesce at 39°C for 0.6% and follow a uniform course up to 2% sodium chloride.

5. Discussion of Supercooling Effect

Now, to examine the variation of the nature of the supercooling type of cyclic variation previously observed in the case of 20 and 30% ethanol solutions,³ in 0.2, 0.4 and 0.9% NaCl solutions⁴ and in solutions^{4,5} of $\text{Sr}(\text{NO}_3)_2$, NH_4NO_3 and KCl, the cooling sequence values of $10^{-3} \times E_n/R$ for all the concentrations of Fig. 2 are separately plotted in Fig. 4, together with the cooling sequence values of pure water (upper solid line curve). It is interesting to note that no supercooling type of effect is observed in the case of water, while such an effect is exhibited by the solutions. It is also seen from graphs of Fig. 4, that the magnitude of

this supercooling type of effect increases progressively with the increase of concentration, and attains a maximum at 1.2%. It then decreases slowly, and the stepwise variation alone appears again in 2% sodium chloride, especially above 27°C, whereas below 27°C a sizeable supercooling type of variation still persists. This shows that in the case of sodium chloride solutions, the supercooling type of effect exists within certain concentration ranges of the solute. It is possible that in and around 3 to 4% concentration, the stepwise variation may reappear clearly throughout the temperature range.

From the above results on the temperature of the jumps as well as the supercooling effect, we may infer that cooperative structural breaking up and reforming occurs within the various sodium chloride solutions, but certain concentrations of NaCl strongly modify the water structure persisting in all these solutions. This may lead to appearance, disappearance, and coalescence of certain

steps with corresponding change in magnitude of the jumps, by an ordering process throughout the volume, as well as possible surface-induced ordering or adsorption in a thin layer. Before theorizing further, it is proposed to obtain more experimental information about the supercooling type of variation by extending the measurements to higher concentrations, up to 5% sodium chloride.

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