

Osmotic and Activity Coefficients of the Sodium Salts of Formic, Acetic and Propionic Acids

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Osmotic and activity coefficients are reported for the sodium salts of formic, acetic and propionic acids to the limits of their solubilities. Hydration of the "second kind" appears to increase with the length of the hydrocarbon chains. The onset of micelle formation is indicated in the more concentrated sodium propionate solutions.

KEY WORDS: Osmotic coefficients; activity coefficients; solvation; micelles; solubility.

1. INTRODUCTION

Osmotic and activity coefficients have been reported⁽¹⁾ for sodium formate and sodium acetate to a concentration of 3.5*m* and for sodium propionate to a concentration of 3.0*m*. The data for sodium acetate have since been extended⁽²⁾ to 6.0*m*. It was brought to this investigator's attention⁽³⁾ that it would be quite useful to extend these data to the limit of solubility of these salts so that they might be used in the preparation of a table of free energies of formation in aqueous solution of organic compounds related to the citric acid cycle.

2. EXPERIMENTAL

Samples of sodium formate and acetate (Fisher certified) were used without further purification. The Fisher purified sodium propionate was recrystallized from distilled water. All salts were dried at 110°C, and stored over P₄O₁₀ in vacuo. As a check on dryness and purity, all osmotic coefficients above 1.0*m* reported for the three salts in Ref. 1 were duplicated with a maximum deviation of 0.002.

Sodium chloride solutions are normally used as reference solutions in isopiestic equilibrations, but for these concentrated solutions, it was necessary to use lithium chloride solutions. The osmotic and ac-

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Table I. Isotonic Solutions

m_{LiCl}	$m_{\text{Na Formate}}$	m_{LiCl}	$m_{\text{Na Acetate}}$	m_{LiCl}	$m_{\text{Na Propionate}}$
2.454	2.943	2.222	2.321	2.171	2.164
2.542	3.074	2.238	2.335	2.383	2.383
2.794	3.437	2.259	2.359	2.637	2.661
3.023	3.774	2.442	2.562	2.845	2.888
3.225	4.082	2.549	2.689	3.035	3.100
3.543	4.590	2.732	2.899	3.449	3.578
4.088	5.517	3.302	3.576	3.987	4.241
4.551	6.338	3.503	3.816	4.779	5.305
4.929	7.062	3.919	4.331	5.349	6.163
5.604	8.491	4.492	5.069	6.073	7.452
6.239	10.047	4.950	5.678	6.095	7.511
6.752	11.425	5.758	6.842	6.288	7.877
7.290	13.018	6.471	7.955	6.744	8.781
7.631	14.158	6.959	8.765	6.875	9.058
7.692	14.378	7.489	9.755	7.010	9.323
7.800	14.744	8.415	11.705	7.357	10.027
		9.066	13.395	7.375	10.075
		9.286	14.074	7.444	10.197
		9.384	14.377		
		9.560	15.009		

tivity coefficients of lithium chloride have been reported by Robinson and Stokes.⁽¹⁾

Solubility data were obtained by removing saturated supernatant solution, evaporating to dryness, and drying the solid at 110°C for 24 hours. Drying the salts in vacuo over P₄O₁₀ yielded identical data.

3. RESULTS AND DISCUSSION

Concentrations of isotonic solutions are reported in Table I. Osmotic and activity coefficients of the three salts are given in Table II. The solubilities of the three sodium salts were found to be: sodium formate, 14.7*m*; sodium acetate, 6.06*m*; and sodium propionate, 10.2*m*. The solubility value for sodium acetate compares quite favorably with data reported by Green⁽⁴⁾ which is interpreted to be about 6.03*m*, and the interpolated value of Morgan⁽⁵⁾ of about 6.00*m*. These are solubilities in equilibrium with the trihydrate salt. There is also a solution which is reported to be 15.2*m* in meta-stable equilibrium⁽⁴⁾ with the anhydrous salt. Our measured concentration for this saturated solution agrees with

Table II. Osmotic and Activity Coefficients

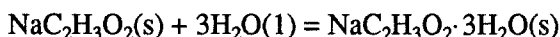
<i>m</i>	Sodium Formate		Sodium Acetate		Sodium Propionate	
	ϕ	γ	ϕ	γ	ϕ	γ
3.0	--	--	--	--	1.256	1.160
3.5	1.022	0.691	1.225	1.057	1.302	1.269
4.0	1.040	0.705	1.269	1.141	1.342	1.380
4.5	1.056	0.720	1.312	1.235	1.375	1.496
5.0	1.071	0.736	1.352	1.334	1.404	1.605
5.5	1.084	0.752	1.389	1.434	1.432	1.711
6.0	1.097	0.769	1.422	1.535	1.452	1.806
6.5	1.110	0.785	1.453	1.637	1.465	1.898
7.0	1.121	0.799	1.481	1.741	1.470	1.984
7.5	1.128	0.811	1.506	1.855	1.472	2.056
8.0	1.133	0.822	1.526	1.957	1.472	2.122
8.5	1.137	0.832	1.545	2.059	1.472	2.183
9.0	1.140	0.842	1.561	2.161	1.476	2.248
9.5	1.142	0.851	1.572	2.254	1.481	2.315
10.0	1.143	0.858	1.580	2.341	1.486	2.384
10.2	--	--	--	--	1.488	2.412
10.5	1.141	0.864	1.587	2.423		
11.0	1.139	0.869	1.591	2.500		
11.5	1.137	0.873	1.591	2.575		
12.0	1.135	0.876	1.589	2.640		
12.5	1.133	0.878	1.584	2.690		
13.0	1.130	0.879	1.576	2.729		
13.5	1.126	0.879	1.566	2.756		
14.0	1.121	0.878	1.554	2.772		
14.5	1.115	0.877	1.540	2.779		
14.7	1.112	0.877	--	--		
15.0			1.525	2.785		
15.2			1.518	2.786		

experimental error with the above reported value.

The osmotic coefficients of the sodium salts of the carboxylic acids are instructive concerning the relative importance of hydrophobic hydration or "hydration of the second kind" and micelle formation. Making use of these data and those of Ref. 1, it is noted that the osmotic coefficients increase regularly with the length of the hydrocarbon chain for 0.1*m* solutions from the formate salt through the caprylate salt. At higher concentrations, however, a reversal occurs and the coefficient of a salt becomes smaller than that of the salt having one fewer carbon

atom. The concentrations at which these reversals occur are: acetate, never; propionate, 7.0*m*; butyrate, 3.5*m*; caproate, 0.9*m*; valerate, 0.8*m*; heptylate, 0.4*m*; and caprylate, 0.4*m*.

These data also permit an interesting calculation for the sodium acetate salts. If the standard solution state is taken as the hypothetical 1.0*m* solution (the usual assumption) and the free energy change for the salt in equilibrium with its saturated solutions, $\Delta G = 0$; one may then calculate the free energy change for the reaction



to be

$$\Delta G = 2RT \ln(m\gamma) (\text{hydrate}) - 2RT \ln(m\gamma) (\text{anhydrous}) = -7.475 \text{ kJ}$$

4. REFERENCES

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