date tridecahydrate has been measured from 0.17 to 4.7°K.

The sample was cooled by adiabatic demagnetization and energy was introduced by means of an amorphous carbon thermometer–heater.

Apparatus has been described for the measurement of adiabatic differential magnetic susceptibility $(\partial I/\partial H)_S$, while the sample is in a field with the usual fluctuations caused by a motor generator supply of current.

The differential susceptibility data for gadolinium phosphomolybdate tridecahydrate presented in a previous research by Giauque and MacDougall have been improved and extended at fields above 1000 gauss.

The intensity of magnetization along six adiabatic paths has been given as a function of magnetic field strength.

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The Apparent and Partial Molal Volumes of the Sodium Salts of Formic, Acetic, Propionic and n-Butyric Acids in Aqueous Solution

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Introduction

The object of this investigation was the determination of the apparent and partial molal volumes of the sodium salts of formic, acetic, propionic and n-butyric acids at different temperatures and concentrations from accurate density measurements in order to ascertain the effect of the increase in chain length upon the change in both the apparent and partial molal volumes. The literature affords but limited data on the densities of aqueous solutions of these salts; in some cases the methods of preparation and of purification are not given. These values are listed in "International Critical Tables,"[1] but the accuracy claimed is usually not better than about 1 part in 1000. Since this accuracy is not sufficient for the evaluation of reliable apparent and partial molal volumes, it was decided to re-determine the densities of solutions of the four salts.

Experimental

The experimental procedure consisted of determining 25, 30, 35 and 40° the densities of aqueous solutions of the salts in a specially designed pycnometer.

The Pycnometer.—Three separate pycnometers of Pyrex glass and of about 50 ml. capacity were employed. They were similar in design to those described by Kelso and Felsing.[2] The pycnometers were calibrated with distilled water (a) under each set of experimental conditions and at 0° and (b) by calibrating at 0° and employing the equation of Felsing and Thomas[3] for the thermal expansion of Pyrex glass:

$$V_T \text{ (Pyrex)} = V_0[0.998325 + 2.316 \times 10^{-7}T + 2.75 \times 10^{-6}T^2 - 2.2 \times 10^{-11}T^3] \quad (1)$$

The two calibrations agreed to at least 1 part in 15,000. The graduated capillaries of the pycnometers were calibrated with mercury; the volume per millimeter of capillary was 0.007 ml. at 0°. Volumes could be read correctly to within 1 part in 15,000.

The Thermostat.—Thermostat temperatures could be held constant to within 0.05° by means of a mercury-in-steel thermoregulator and a sensitive relay system controlling a 75-watt heater. Temperatures were determined by a long mercurial thermometer of short range calibrated by the National Bureau of Standards.

Weight Determinations.—Calibrated weights were employed; the balance had a Pregl sensitivity of better than 25 and weighings could be reproduced to better than 0.05 mg.; all weights were corrected to a vacuum.

Materials. (a) Sodium Formate and Sodium Acetate.— C. P. salts were recrystallized three times from conductivity water. (b) Sodium Propionate.—Weighed equivalent quantities of highly purified sodium carbonate and of propionic acid ($n^{19.5}$D, 1.3874; "I. C. T." value,[4] $n^{19.5}$D, 1.38736) were allowed to react in solution. The temperature was raised, after reaction, to 90° to expel the carbon dioxide from the solution. (c) Sodium Butyrate.—This salt was prepared by the interaction of pure sodium carbonate and butyric acid (m. p., −8.0°; Heilbron,[5] −8.0°). (d) Solutions.—Concentrated stock solutions of these salts were analyzed by treatment of a proper-sized sample with a slight excess of c. p. sulfuric acid in a platinum crucible. The sodium sulfate residue, after careful evaporation and heating to low red heat, had a weight of approximately 0.5 g. or over; analyses were made in triplicate and checked to better than 0.05%. All dilutions of this stock solution were made by weight. (e) Water.—All water used had a specific conductance of 1.0×10^{-6} reciprocal ohms.

The Experimental Data.—All solutions were introduced into the pycnometer by means of a long, thin capillary; the filled pycnometer was weighed at room temperature

(1) "I. C. T.," Vol. 3, p. 83; ibid., Vol. 7, p. 74.
(2) Kelso with Felsing, THIS JOURNAL, 60, 1949 (1938).
(3) Felsing and Thomas, Ind. Eng. Chem., 21, 1269 (1929).
(4) "I. C. T.," Vol. 7, p. 35.
(5) Heilbron, "Dictionary of Organic Compounds," Vol. 1, Oxford University Press, New York, N. Y., 1934, p. 222.

and the volume of the solution was read on the graduated capillary after the closed pycnometer had remained in the thermostat for forty-five minutes or more. Check readings were made at fifteen minute intervals for another hour. The thermostat temperature was then raised to the next higher point and the process repeated.

Treatment of Results

The apparent molal volumes were calculated from the observed densities by means of the relation proposed by Gucker[6]

$$\phi(V_2) = \frac{1000}{c} - \frac{1}{d_1}\left[\frac{1000d}{c} - M_2\right] \quad (2)$$

The apparent molal volumes thus obtained were plotted on suitable scale against $c^{1/2}$; the curves obtained were found, as predicted by Masson,[7] to be linear up to the concentrations listed in the paragraph following Table II, after which the points drifted upward from the straight line. The few points in the concentrated region which were not on the straight line were omitted in determining the linear relation of $\phi(V_2)$ *versus* $c^{1/2}$

$$\phi(V_2) = \phi°(V_2) + \frac{\partial\phi(V_2)}{\partial c^{1/2}}c^{1/2} \quad (3)$$

The method of "zero sum" of Campbell[8] was used obtaining these linear relations. From these relations, the density equations of Table I were derived and the partial molal volumes were calculated by the relation of Gucker[6]

$$V_2 = \phi°(V_2) + \frac{[3000 - c\phi°(V_2)]}{\left[2000 + c^{3/2}\dfrac{\partial\phi(V_2)}{\partial c^{1/2}}\right]}\frac{\partial\phi(V_2)}{\partial c^{1/2}}c^{1/2} \quad (4)$$

where $\phi°(V_2)$ is the apparent molal volume at zero concentration, and $\phi(V_2)$ is defined as originally proposed by Lewis and Randall.[9]

The densities[10] of the solutions investigated may be represented by equations of the form

$$d \text{ (g./ml.)} = d_0 + Ac - Bc^{1/2}$$

In Table I are presented the values of the constants for the equations for the four salts at each of the four temperatures. Observed values of the density are reproduced by these equations to *at least* 1 part in 10,000.

The constants for Equations (3) and (4) by means of which the apparent and partial molal volumes may be calculated are presented in Table

(6) Gucker, *J. Phys. Chem.*, **38**, 307 (1934).

(7) Masson, *Phil. Mag.*, [7] **8**, 218 (1929).

(8) Campbell, *ibid.*, [7] **47**, 816 (1924).

(9) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Company, New York, N. Y., 1923, p. 35.

(10) Original density data may be found in a Master of Science thesis submitted by George M. Watson in August, 1940, to the Graduate Faculty of the University of Texas.

TABLE I

CONSTANTS FOR THE EQUATIONS RELATING DENSITY TO CONCENTRATION

	Temp.(°C.)	25°	30°	35°	40°
	d_0	0.99707	0.99567	0.99406	0.99224
NaHCOO (8 det.;	A	.04349	.04317	.04293	.04253
0.3 to 2.6 moles/l.)	B	.00227	.00226	.00225	.00207
NaCH₃COO (19 det.;	A	.04340	.04292	.04272	.04261
0.3 to 3.0 moles/l.)	B	.00250	.00237	.00238	.00240
NaC₂H₅COO (14 det.;	A	.04340	.04296	.04267	.04239
0.3 to 3.0 moles/l.)	B	.00269	.00263	.00262	.00262
NaC₃H₇COO (14 det.;	A	.04188	.04168	.04142	.04104
0.3 to 2.0 moles/l.)	B	.00256	.00277	.00289	.00292

II together with the increments in $\phi°(V_2)$ due to an increase in chain length of a CH_2 grouping.

TABLE II

CONSTANTS FOR THE APPARENT AND PARTIAL MOLAL VOLUME EQUATIONS

Temp.,°C.	Salt, sodium	$\phi°(V_2)$	$\dfrac{\partial\phi(V_2)}{\partial c^{1/2}}$	$\dfrac{\Delta\phi°(V_2)}{(\text{ml.})}$
25	Formate	24.60	2.28	
	Acetate	38.75	2.53	14.15
	Propionate	52.82	2.70	14.07
	Butyrate	68.41	2.57	15.59
30	Formate	24.95	2.27	
	Acetate	39.29	2.38	14.34
	Propionate	53.34	2.64	14.05
	Butyrate	68.71	2.78	15.37
35	Formate	25.24	2.26	
	Acetate	39.55	2.39	14.31
	Propionate	53.72	2.64	14.17
	Butyrate	69.08	2.91	15.36
40	Formate	25.69	2.09	
	Acetate	39.74	2.42	14.05
	Propionate	54.10	2.64	14.36
	Butyrate	69.59	2.94	15.49

The range of applicability of these equations is 0.3 to 2.6 molal (or higher, possibly) for the sodium formate, 0.3 to 3.0 M for the acetate; 0.3 to 2.7 M for the propionate, and 0.3 to 2.0 M for the butyrate; over these concentration ranges the apparent molal volume is a linear function of $c^{1/2}$. The experimental determinations in the concentrated region, where the density begins to deviate from the linear relation, are too few in number to warrant the addition of an extra term to the apparent molal volume–concentration relation.

Discussion of Results

It has been determined that Masson's law[7] is obeyed by the four salts over a considerable concentration range, as indicated, within an accuracy of 0.01% in the density determinations. Such an accuracy does not reveal any real curvature in the $\phi(V_2)$ *versus* $c^{1/2}$ relation, though greater pre-

cision than 1 part in 10,000 might do so. The values for $\phi^\circ(V_2)$ in Table II are given to 0.01 ml.; these values are the resultants of the equations based upon the experimental points. In view of the uncertainties of determining $\phi(V_2)$ values, it is not claimed that $\phi^\circ(V_2)$ values are known to better than 0.05 to 0.1 ml.

Redlich[11] has developed a relation between $\phi(V_2)$ and $c^{1/2}$ based upon the Debye–Hückel theory, for electrolytes

$$\phi(V_2) = \phi^\circ(V_2) + kw^{3/2}c^{1/2}$$

Here $w = \frac{1}{2}\Sigma\nu_i z_i^2$, ν_i being the number of ions of species i formed by one molecule of the electrolyte and z_i, the valence of the ion. He finds that for uni-univalent electrolytes, such as potassium chloride, the value of k (the slope of the $\phi(V_2)$ vs. $c^{1/2}$ line as infinite dilution is approached) is approximately 1.86. The data of the present investigation do not include the extremely dilute region; hence it is not possible to use these data for a test of the Redlich relation. The $\partial\phi(V_2)/\partial c^{1/2}$ values given in Table II are higher than Redlich's value of 1.86, but it should be remembered that they are applicable to the region 0.3 to 3.0 (approx.) molal and do not necessarily apply to the region below and including 0.1 molal.

The values obtained for the densities of the sodium acetate solutions do not agree with those listed in the "International Critical Tables,"[1] the values there listed being consistently lower than those of this investigation. The difference is about 0.08% in a 1 molar to 0.16% in a 2 molar solution. On account of this difference, the densities of sodium acetate were carefully redetermined from new material and new stock solutions, carefully analyzed; however, the results agreed with the previous results to 0.01%.

The density data of this investigation fall in the order: formate, acetate, propionate, butyrate;

(11) Redlich, J. Phys. Chem., 44, 619 (1940).

the use of "I. C. T." data for sodium acetate would place the acetate densities below those of the sodium propionate solutions, which order seems improbable.

Masson[7] stated that sodium acetate did not follow his straight line law; the data of this investigation show that it follows the linear law over the range 0.3 to 3.0 molar. It has been impossible to locate the data upon which Masson based his statement regarding sodium acetate.

The $\Delta\phi^\circ(V_2)$ values listed in Table II show a mean value of approximately 14.6 ml. per CH_2 increase at infinite dilution; the variation is essentially within the accuracy of the determinations of the density. This mean value of 14.6 ml. is somewhat less than the value of 16.3 ml. used by Cohn[12] for the CH_2 increase of certain aliphatic and amino acids at 0.25 molal aqueous solution. It has been noted that the partial molal volumes of ionized substances are found to be smaller than would be expected from the values of the partial molal volumes of the groups making up the compound. However, even this would not explain the observed difference.

Summary

1. The densities of aqueous solutions of the sodium salts of formic, acetic, propionic and n-butyric acids have been determined at four temperatures.

2. The apparent and partial molal volumes have been calculated and expressed by means of equations.

3. The apparent molal volume of the methylene group has been found to be approximately 14.6 ml. at infinite dilution, increasing slightly with increasing concentration.

(12) Cohn, McMeekin, Edsall and Blanchard, THIS JOURNAL, 56, 784 (1934).