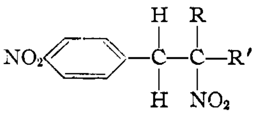
TABLE I

p-NITROBENZYL DERIVATIVES OF THE NITRO PARAFFINS

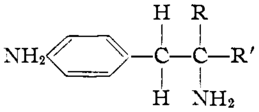


Derivative of	Yield, %	M. p., °C.	Formula	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
Nitroethane,[a] R = H, R′ = CH_3	24.4	51–52	$C_9H_{10}O_4N_2$						
1-Nitropropane, R = H, R′ = C_2H_5[b]	50.5	64–65	$C_{10}H_{12}O_4N_2$					12.50	12.40
2-Nitropropane, R = CH_3, R′ = CH_3	52.9	65–66	$C_{10}H_{12}O_4N_2$	53.57	53.84	5.36	5.45	12.50	12.43
1-Nitrobutane, R = H, R′ = C_3H_7	37.5	44–46	$C_{11}H_{14}O_4N_2$	55.46	55.72	5.88	6.09	11.76	11.67
2-Nitrobutane, R = CH_3, R′ = C_2H_5	39.8	58–60	$C_{11}H_{14}O_4N_2$	55.46	55.60	5.88	5.62	11.76	11.50
Nitrocyclopentane, RR′ = cyclopentyl	58.9	89–90	$C_{12}H_{14}O_4N_2$	57.60	57.77	5.60	5.72	11.20	11.26
Nitrocyclohexane, RR′ = cyclohexyl	62.3	98–100	$C_{13}H_{16}O_4N_2$	59.09	58.82	6.06	6.00	10.51	10.48

[a] This compound was first prepared and identified by Hoover.[7] [b] This compound was prepared by Dunning[6] and by Hoover.[7]

TABLE II

DIAMINES FROM *p*-NITROBENZYL DERIVATIVES,



Derivative of	Yield, %	B. p., °C.	B. p., Mm.	M. p., °C.	$n^{20}D$	Formula	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
Nitroethane,[a] R = H, R′ = CH_3	70.1	114	1.5	....	1.5742	$C_9H_{14}N_2$						
1-Nitropropane, R = H, R′ = C_2H_5	74.4	110	1	....	1.5642	$C_{10}H_{16}N_2$					17.07	17.00
2-Nitropropane, R = CH_3, R′ = CH_3	93.3	...	...	84–85	....	$C_{10}H_{16}N_2$	73.17	72.93	9.76	9.88	17.07	16.98
1-Nitrobutane, R = H, R′ = C_3H_7	82.5	143	3	....	1.5533	$C_{11}H_{18}N_2$					15.73	15.32
2-Nitrobutane, R = CH_3, R′ = C_2H_5	50.9	128	1.5	....	1.5600	$C_{11}H_{18}N_2$	74.16	74.02	10.11	10.22	15.73	15.90
Nitrocyclopentane, RR′ = cyclopentyl	65.9	125	3	....	1.5808	$C_{12}H_{18}N_2$					14.74	14.88
Nitrocyclohexane, RR′ = cyclohexyl	86.5	...	...	98–100	....	$C_{13}H_{20}N_2$	76.47	76.43	9.80	9.74	13.73	13.80

[a] This compound was first prepared by Hoover[7].

Summary

A series of dinitro compounds has been prepared by the reaction of the sodium salts of primary and secondary nitro paraffins with *p*-nitrobenzyl chloride. These dinitro compounds have been reduced to diamines by high pressure catalytic hydrogenation.

LAFAYETTE, INDIANA RECEIVED JANUARY 20, 1949

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY OF MICHIGAN STATE COLLEGE]

The Apparent Molal Volume of Strontium Chloride in Ethanol–Water Mixtures

BY RICHARD LOUIS BATEMAN

Measurements made in this Laboratory[1] have shown that the conductance curves (equivalent conductance as a function of solvent composition) for strontium chloride in ethanol–water mixtures give points of inflection at about 60% ethanol in the solvent. This may be attributed to simultaneous changes in the viscosity and dielectric constant of the solvent as well as to changes in the degree of solvation of the ions of the electrolyte as the composition of the solvent is varied. When solvation of the ions of a salt occurs, the solvent molecules of the ion–solvent complex may be assumed to be more closely packed than in the pure solvent.[2] This packing effect should influence the molal volume of the salt; the greater the packing the smaller the molal volume. Thus the molal volume of the salt should be a measure of the size of the ion–solvent complex. The present work was undertaken to determine the influence of solvent composition and solute concentration on solution density and apparent molal volume of strontium chloride in various ethanol–water mixtures at 25°. No previous work has been reported on the apparent molal volume of strontium chloride in ethanol–water mixtures.

Experimental Part

Preparation of Materials.—J. T. Baker C. P. strontium chloride heptahydrate was recrystallized once above and once below 61.34° by the method of Richards and Yngve[3] and oven dried to constant weight.

Ethyl alcohol was freed of amines by treating each liter of stock 95% alcohol with a solution containing 20 ml. of sulfuric acid and 20 ml. of water and then distilling. Al-

---

[1] Bateman and Ewing, THIS JOURNAL, **70**, 2137 (1948).

[2] Longsworth and MacInnes, *J. Phys. Chem.*, **43**, 239 (1939).

[3] Richards and Yngve, THIS JOURNAL, **40**, 91 (1918).

dehydes were removed from the distillate by treating with alcoholic lead acetate[4] (3 g. of lead acetate in 5 ml. of water then 5 g. of potassium hydroxide in 25 ml. of alcohol and distilling). Absolute alcohol was then prepared by refluxing and distilling from quick lime (200 g. per liter).

Conductance water was prepared by the redistillation of water containing a little potassium permanganate through a block tin condenser.

The ethanol–water solvents were prepared by the weight method and the exact composition determined by density measurements and interpolation of these values with those from the "International Critical Tables."[5]

The strontium chloride solutions in ethanol–water mixtures were prepared from anhydrous strontium chloride by the weight method correcting to vacuum and expressing concentrations in terms of gram-moles of strontium chloride per 1000 g. of solvent.

Apparatus and Procedure.—The density measurements were made in pycnometers having volumes of 48.6358 and 49.9462 ml. at 25°. These were made from 50-ml. glass-stoppered volumetric flasks by replacing a portion of the neck with a capillary tube of about 0.7 mm. inside diameter. The pycnometers were calibrated using freshly prepared conductance water at 25.00° and considering the density of water at this temperature as 0.9970739 g./ml. The filling device for the pycnometers was essentially the same as described by Reilly and Rae.[6] The density determinations were all made at 25° in a water-filled thermostat bath which was constant to within 0.01° during the series of measurements. The bath temperature was determined with a thermometer that had been certified by the Bureau of Standards (certificate No. 49571). The temperature fluctuations were followed with a Beckmann thermometer.

With the aid of the filling device, the pycnometer was rinsed several times with conductance water and dried by placing in warm water and evacuating for a few minutes. The pycnometer was then filled with the solution and placed in the thermostat bath for at least thirty minutes. The upper inside portion of the pycnometer was then dried with folded filter paper and the liquid in the capillary stem brought to the mark with the aid of a fine glass capillary tube. Check determinations were made for each concentration using completely independent solutions. Precautions were taken to minimize the exposure of the solutions to the atmosphere.

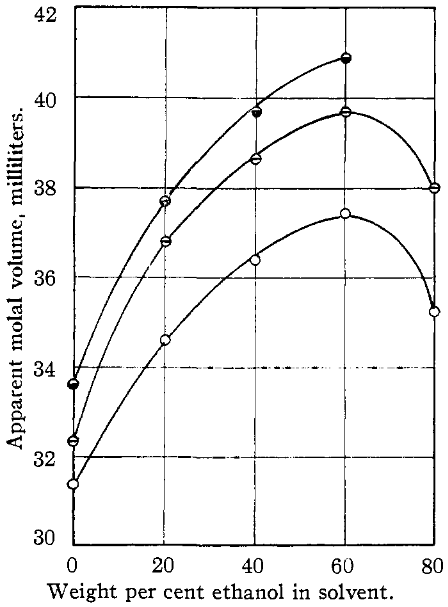


Fig. 1.—Apparent molal volume of strontium chloride in ethanol–water mixtures at 25°: ○, 0.1 molal; ⊖, 0.2 molal; ◓, 0.5 molal strontium chloride solutions.

Results and Discussion

Table I gives the experimentally determined densities of solutions of strontium chloride in ethanol–water mixtures and the corresponding apparent molal volumes of strontium chloride in these solutions at 25°. The ethanol percentages in the table refer to the percentages of ethanol by weight in the solvent. Each value given in the table was obtained from the average of two independent determinations that had been interpolated to "round" solvent composition and solute concentration. Figure 1 shows the influence of solvent composition on the apparent molal volume of strontium chloride for three concentrations.

Table I

Apparent Molal Volume of Strontium Chloride in Ethanol–Water Mixtures at 25°

Molality of SrCl$_2$	Density of soln., g./ml.	Vol. of soln. per 1000 g. solvent, ml.	Apparent molal vol. SrCl$_2$, ml.
0% Ethanol			
0.5	1.05839	1019.74	33.62
.4	1.04665	1016.02	32.73
.3	1.03450	1012.64	32.36
.2	1.02223	1009.27	31.72
.1	1.00973	1006.06	31.37
0	0.99708	1002.93	
20% Ethanol			
.5	1.02434	1053.63	37.70
.4	1.01318	1049.58	37.01
.3	1.00166	1045.83	36.83
.2	0.99005	1042.08	36.49
.1	.97844	1038.24	34.60
0	.96639	1034.78	
40% Ethanol			
.5	.98707	1093.41	39.70
.4	.97626	1089.28	39.29
.3	.96536	1085.15	38.64
.2	.95431	1081.10	37.72
.1	.94305	1077.20	36.40
0	.93148	1073.56	
60% Ethanol			
.5	.94025	1147.86	40.90
.4	.92992	1143.56	40.37
.3	.91947	1139.31	39.68
.2	.90885	1135.18	38.86
.1	.89807	1131.15	37.44
0	.88699	1127.41	
80% Ethanol			
.4	.88088	1207.22	38.71
.3	.87069	1203.14	38.01
.2	.86039	1199.12	36.89
.1	.84990	1195.26	35.24
0	.83911	1191.74	

---

[4] S. Kiczales, *Ind. Eng. Chem.*, **20**, 493 (1928).

[5] "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., 1928, Vol. III, p. 116.

[6] Reilly and Rae, "Physico-Chemical Methods," D. Van Nostrand Co., New York, N. Y., 1939, Vol. I, p. 492.

The volume of solution containing 1000 g. of solvent increases continuously as the concentration of strontium chloride increases. Also the rate at which this volume increases with respect to the concentration (partial molal volume) is greatest for the solvent containing 60% ethanol. The apparent molal volume of strontium chloride in a given solvent is greatest in the most concentrated solution. This indicates, for these systems, that for a given solvent the extent of solvation for the individual ions is least when the largest number of ions is present or when the number of solvent molecules for each ion is least. (The ion–solvent complex should be less compact or smaller in size if the solvent dipoles have been partially reduced by the presence of other ions in the solution and the greater this reduction the less the extent of solvation and the greater the apparent molal volume). This may be observed from Fig. 1. It may also be noted from Fig. 1 that the apparent molal volume of strontium chloride (for each concentration) reaches a maximum when the solvent contains about 60% ethanol. At points where these maxima are reached the degree of solvation should be least with greater solvation occurring both above and below these points.

Summary

1. The densities of solutions of strontium chloride in different mixtures of ethanol and water at 25° have been determined.

2. The apparent molal volumes of strontium chloride in mixtures of ethanol and water have been calculated and the results discussed.

3. The apparent molal volumes of strontium chloride in ethanol–water mixtures exhibit a maximum in solutions containing about 60% ethanol and this volume is greatest in the most concentrated solutions.

EAST LANSING, MICHIGAN RECEIVED FEBRUARY 7, 1949

[CONTRIBUTION NO. 15 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

Hydrazine: Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure, Entropy and Thermodynamic Functions[1]

BY D. W. SCOTT, G. D. OLIVER,[1a] MARGARET E. GROSS, W. N. HUBBARD AND HUGH M. HUFFMAN

Because of the potential use of hydrazine as a rocket propellant, a knowledge of its thermodynamic properties is of considerable importance. Consequently, the Thermodynamics Laboratory of the Petroleum and Natural-Gas Branch of the Bureau of Mines has undertaken the measurement and computation of certain of these properties. This paper reports the results of calorimetric and vapor-pressure measurements which yield a value of the entropy of hydrazine vapor and also presents a tabulation of various thermodynamic functions calculated from spectroscopic and molecular structure data.

Experimental

Heat Capacity.—The measurements were made in the adiabatic calorimeter apparatus first described by Ruehrwein and Huffman.[2] The hydrazine used for this work was obtained from the Western Cartridge Co. through the courtesy of R. L. Womer, and as received had a purity of about 99.2 mole per cent., the major contaminant being water. It was further purified by refluxing over barium oxide, followed by repeated fractional crystallization. From a study of the melting point as a function of the fraction melted the purity of the sample was estimated to be 99.75 mole per cent. The melting point of the actual sample was found to be 274.56°K. and that calculated for the pure material was 274.69°K.

In the heat capacity measurements, the absorption of a small amount of heat (about 8 cal./mole) was observed to occur near 220°K. This presumably resulted from the melting of a eutectic mixture of hydrazine and hydrazine monohydrate formed from water impurity in the sample. Semishin,[3] who studied the freezing-point behavior of the hydrazine–water system, was unable to measure this eutectic temperature because of excessive supercooling, but any reasonable extrapolation of his freezing point curves at higher temperatures gives an intersection at about the temperature where this absorption of heat was observed.

The precision of the calorimetric measurements was approximately 0.1% above 30°K., but because of the relatively impure sample used and certain difficulties encountered in the measurements, the absolute uncertainty of the heat-capacity values may be as great as 0.3%. Because the heat-capacity data are less accurate than is usual for this type of work and because the true course of the heat-capacity curve between about 200°K. and the melting point is obscured by the premelting effect, it seemed desirable to report only the smoothed values of heat capacity at integral temperatures. These are listed in Table I. Two concordant values were obtained for the heat of fusion. After applying approximate corrections

---

[1] Not subject to copyright.

[1a] Present address: Carbide & Carbon Chemicals Corp., Oak Ridge, Tenn.

[2] Ruehrwein and Huffman, THIS JOURNAL, **65**, 1620 (1943).

[3] Semishin, *J. Gen. Chem.* (*U. S. S. R.*), **8**, 654 (1938).