deformation is probably of low intensity in these compounds, but several unsymmetrical ring deformations are possible in each.

Lankelma and his co-workers[3] use absorptions at 9.75 and 11.55 μ, reported as being typical of cyclopropane itself, for purposes of identifying 1,1,2-trimethylcyclopropane and evaluating its purity. It may be seen from our spectrograms of substituted cyclopropanes that a strong absorption does not occur consistently at 11.6 μ. This wave length region is thus less useful than the 9.9 μ band for purposes of characterization.

Cyclobutane Derivatives.—The spectra of all of the cyclobutanes presented in Fig. 1 (Nos. 15 to 21), show a prominent absorption band peaked at 10.9 to 11.0 μ; this band seems to be characteristic of the cyclobutane ring. In the spectrum of cyclobutane itself, Wilson[2d] found in this region an absorption band which he assigned to two methylene rocking frequencies (903 and 923 cm.$^{-1}$). It remains to be seen whether the band at 10.9 to 11.0 μ will appear with equal regularity in the spectra of cyclobutane molecules having substitution on all of the ring carbon atoms.

Acknowledgment.—The authors acknowledge their indebtedness to R. Bowling Barnes (American Cyanamid Company), H. H. Nielsen and R. A. Oetjen (both of the Ohio State University), Forrest F. Cleveland (Illinois Institute of Technology) and R. F. Marschner (Standard Oil Company of Indiana) for their advice and criticisms at various points of this investigation. Thanks are extended to K. W. Greenlee for his sustained interest in this work and for his supervision of the preparation of many of the samples used. The work reported herein was sponsored by the American Petroleum Institute (Research Project 45) in coöperation with the Ohio State University Research Foundation.

Summary

The infrared absorption spectrograms of fourteen individual cyclopropane hydrocarbons and seven individual cyclobutane hydrocarbons have been determined.

A prominent absorption band peaked at about 9.9 μ has been noted in the spectra of all of the cyclopropanes examined; similarly, a pronounced band peaked at about 11.0 μ has been noted in the spectra of all the cyclobutanes. These bands are suggested as being useful in identifying such ring structures.

COLUMBUS, OHIO RECEIVED DECEMBER 13, 1948

[CONTRIBUTION NO. 712 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Heats of Dilution of Aqueous Sodium Bromide and the Standard Heat of Solution of Sodium Bromide at 25°

BY W. E. WALLACE

In the course of a recent study dealing with sodium chloride–sodium bromide solid solutions,[1] a reliable value for the standard heat of solution of sodium bromide was required. After consulting the literature it became evident that the several earlier investigations of the thermal properties of sodium bromide solutions were not sufficiently complete to permit a trustworthy evaluation of its standard heat of solution. The data reported in this paper include a series of measurements of the heats of solution of sodium bromide, and also the heats of dilution of aqueous sodium bromide solutions from saturation (9.192 molal) to 0.002 molal. When these data are combined with the information provided by Hammerschmid and Robinson[2] for extremely dilute sodium bromide solutions, a precise evaluation of the standard heat of solution can be made. In addition, the heat of dilution determinations for concentrated solutions permit a more satisfactory evaluation of the partial molal heat contents at high concentrations than has heretofore been possible.

Experimental.—The calorimeter used in this study has been described.[1] During the solution experiments the calorimeter vessels were provided with devices for crushing the thin glass bulbs used to contain the salt sample to be dissolved. Coincident with the breaking of the bulb containing the sample in one calorimeter vessel, an empty bulb in the other calorimeter vessel was broken to compensate for the very small heat of crushing. Blank experiments (neither side containing a sample) showed that this method for nullifying the heat of crushing was completely effective.

When the calorimeter was used to measure heats of dilution, the crushing devices were replaced with gold-plated brass pipets having volumes of 6.788 and 6.755 ± 0.004 ml. The calorimeter vessels contained 1000 and 1005 ± 1 ml. of water, respectively. The technique employed in measuring heats of dilution has been described in earlier communications from this Laboratory.[3,4]

The sodium bromide employed in this study was

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[1] M. Fineman and W. E. Wallace, THIS JOURNAL, **70**, 4165 (1948).

[2] H. Hammerschmid and A. L. Robinson, *ibid.*, **54**, 3120 (1932).

[3] E. Lange and A. L. Robinson, *Chem. Revs.*, **9**, 89 (1931).

[4] W. E. Wallace and A. L. Robinson, THIS JOURNAL, **63**, 958 (1941).

part of the sample prepared for use in the determinations of the heats of formation and lattice spacing of sodium chloride–sodium bromide solid solutions.[1,5] It was prepared from Eimer and Amend Tested Purity sodium oxalate and purified bromine by the method of Baxter and Grover.[6] Gravimetric analysis showed that its bromide content was 99.93% of the theoretical value.

All solutions were made up on a weight basis. The number of moles contained in the dilution pipets was calculated with the aid of the density data given in the "International Critical Tables."

Experimental Results.—The heat of solution determinations are summarized in Table I. Molalities in the fourth column refer to the final concentration in the solution process. The heats of dilution listed in column 5 were computed using the equation developed by Young and Seligmann[7] to represent Hammerschmid and Robinson's experimental data.

The heat of dilution data are presented in Table II. Initial and final concentrations are listed in columns 1 and 2, respectively. The measured heats of dilution are given in column 4. In column 5 are listed values for the additional heat that would be developed in diluting the solution of concentration m_2 to infinite dilution. The quantities in column 5 were obtained from Hammerschmid and Robinson's data as described above. The apparent relative heat contents of the solute (ϕL_2) at the several concentrations are shown in column 6.

The ϕL_2 values have been represented analytically by an expression of the form

$$\phi L_2 = Am^{1/2}\,(1 + Be^{-\mathrm{cm.}^{1/2}}) + Dm + Em^{3/2} \quad (1)$$

To evaluate the five constants of equation (1), the following procedure was used. B was expressed in terms of A by imposing the condition that the limiting Debye–Hückel slope (481)[8,9] must be attained as the (square root of) molality approaches zero. The remaining four constants were determined from the experimental data. The values of the constants are: $A = 343.58$, $B = 481/A - 1 = 0.400$, $C = 2.99$, $D = -512.495$, $E = 105.915$. The equation appears to afford a fairly satisfactory representation of the data for the entire composition range, from infinite dilution to saturation. Below 0.01 molal, it agrees to better than one cal./mole with the very precise equation obtained by Young and Seligmann. Equation (1) reproduces both the data obtained in this study and the results of Hammerschmid and Robinson with an average deviation of about 2 cal./mole.

Relative Partial Molal Heat Contents.—The $\overline{L}_1$'s and $\overline{L}_2$'s are conveniently obtained from ϕL_2's using the equations developed by Rossini[10]

$$\overline{L}_1 = -\frac{m^{3/2}}{2(55.508)}\,\frac{\mathrm{d}(\phi L_2)}{\mathrm{d}m^{1/2}}. \quad (2)$$

$$\overline{L}_2 = \phi L_2 + \frac{m^{1/2}}{2}\,\frac{\mathrm{d}(\phi L_2)}{\mathrm{d}m^{1/2}} \quad (3)$$

Introducing equation (1) into these expressions and making use of the values of the constants given above, the following relationships are obtained.

$$\overline{L}_1 = -3.0949m^{3/2}[1 + 0.400e^{-2.99m^{1/2}}\,(1 - 2.99m^{1/2})] + 9.2328m^2 - 2.8622m^{5/2} \quad (4)$$

$$\overline{L}_2 = 515.37m^{1/2} + 137e^{-2.99m^{1/2}}\,(1.500m^{1/2} - 1.495m) - 1024.99m + 264.788m^{3/2} \quad (5)$$

In Table III values of $\overline{L}_1$, $\overline{L}_2$, and ϕL_2 computed

TABLE I

HEATS OF SOLUTION OF SODIUM BROMIDE IN WATER AT 25°

NaBr dissolved, mole	Integral heat of solution			ΔH	
	cal.	cal./mole NaBr	m_f	ΔH ($m_f \rightarrow 0$) cal./mole	ΔH_0 NaBr
0.02985	−2.69	−90	0.02976	−57	−147
.04725	−3.48	−74	.04711	−65	−139
.04774	−3.91	−82	.04788	−65	−147
.05368	−4.10	−76	.05384	−67	−143
.06062	−4.35	−72	.06080	−69	−141
.06445	−4.91	−76	.06464	−70	−146
				Average	−144

TABLE II

HEATS OF DILUTION OF AQUEOUS SODIUM BROMIDE SOLUTIONS AT 25°

m_1	m_2	Experiments	ΔH	ΔH ($m_2 \rightarrow 0$) cal./mole	ϕL_2 NaBr
0.2545	0.001719	4	− 54 ± 1	−18	72
0.6296	.004211	4	+ 13 ± 0.7	−30	17
1.567	.01016	4	+203 ± .5	−39	−164
2.909	.01806	4	+430.6 ± .7	−48	−383
4.111	.02497	2	+578.2 ± .7	−54	−524
5.469	.03195	3	+702.0 ± .5	−58	−644
6.835	.03876	2	+774.4 ± .5	−61	−713
7.884	.04344	2	+794.1 ± .7	−63	−731
9.004	.04830	2	+787.8 ± .8	−65	−723

TABLE III

PARTIAL AND APPARENT MOLAL HEAT CONTENTS OF AQUEOUS SODIUM BROMIDE SOLUTIONS AT 25°

$m^{1/2}$	$\overline{L}_1$ cal./mole H_2O	$\overline{L}_2$ cal./mole NaBr	ϕL_2 cal./mole NaBr
0.01	$-\ 0.0_5417$	7.0	4.7
.05	$-\ 0.0_3444$	31.7	21.8
.1	$-\ .0_2284$	55.3	39.5
.5	+ .117	46.0	72.2
1.0	3.39	−245	− 56.1
1.5	14.7	−641	−278
2.0	31.5	−952	−515
2.5	32.9	−981	−689
3.0	−31.1	−530	−722
3.032 (satd.)	−39.4	−480	−717

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(5) J. E. Nickels, M. Fineman and W. E. Wallace, *J. Phys. and Colloid Chem.*, **53**, 625 (1949).

(6) G. P. Baxter and F. L. Grover, THIS JOURNAL, **37**, 1027 (1915).

(7) T. F. Young and P. Seligman, *ibid.*, **60**, 2379 (1938).

(8) O. Gatty, *Phil. Mag.*, **11**, 1082 (1931).

(9) G. Scatchard, THIS JOURNAL, **53**, 2037 (1931).

(10) F. D. Rossini, *Bur. Standards J. Research*, **4**, 313 (1930).

from equations (1), (4) and (5) at several rounded concentrations are given.

Comparison of the Heats of Solution with the Results of Other Investigations.—Values for the standard heat of solution of sodium bromide have been reported by Wust and Lange[11] and by Hammerschmid and Robinson.[2] Bichowsky and Rossini[12] have given a value for the heat of solution of sodium bromide in 200 moles of water. Wust and Lange measured heats of solution of sodium bromide at concentrations ranging from near saturation to about 1 molal. Extrapolating their results, they obtained a value of 0 cal./mole at infinite dilution. Wust and Lange's extrapolation was grossly in error as later heat of dilution studies[2] at high dilutions have shown.[13] Hammerschmid and Robinson utilized their heats of dilution, together with Wust and Lange's results, to obtain a ΔH^0 of -44 cal./mole. This result is open to question for two reasons. There is a sizeable gap between the two sets of data and considerable uncertainty unavoidably enters in combining them, especially since the slope is changing rapidly in the region where data are lacking. Furthermore, a numerical error seems to have crept into Hammerschmid and Robinson's paper, since a recalculation of the standard heat of solution using their heat of dilution curves gives a value for ΔH^0 of -185 cal./mole. Bichowsky and Rossini tabulate a heat of solution for sodium bromide which appears to be based largely on Wust and Lange's work with a little weight given to some older studies. Correcting Bichowsky and Rossini's datum to infinite dilution and 25°, one obtains a ΔH^0 of $+323$ cal./mole. This value appears to be inconsistent with its sources and must be considerably in error.

If the heat of dilution data presented in this paper are used to extrapolate the results of Wust and Lange, a value of -155 cal./mole is found for ΔH^0. This is in reasonably good agreement with the mean value for ΔH^0 obtained in the present study, namely, -144 cal./mole.

A general comparison of Wust and Lange's data with the results of this study is offered in Fig. 1. The full line is computed from equation (1). Relative apparent molal heat contents were calculated from Wust and Lange's determinations by taking the ϕL_2 for a solution 7.835 molal to be -730 cal./mole (as computed from equation (1)) and computing other ϕL_2 from the observed differences in their measured heats of solution. The results so obtained agreed on the average with equation (1) to better than 2 cal./mole.

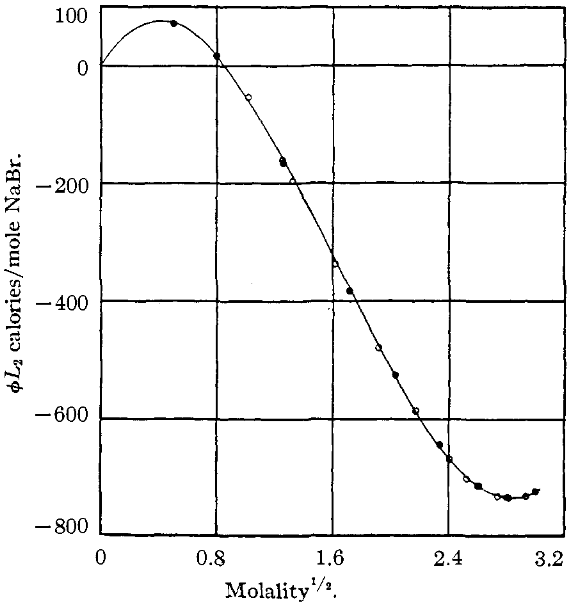

Fig. 1.—Graph showing the relative apparent molal heat contents of sodium bromide as a function of concentration: O, Wust and Lange; ●, this research; —, equation (1).

Summary

The heats of dilution of sodium bromide at 25° have been measured between saturation (9.192 molal) and 0.002 molal. These data have been combined with similar measurements at high dilutions to give a heat of dilution curve for the entire concentration range. Using this curve and six determinations of the heats of solution of sodium bromide, the standard heat of solution is found to be -144 cal./mole. Using the same heat of dilution curve, the results of Wust and Lange yield a value of -155 cal./mole for the standard heat of solution.

PITTSBURGH 13, PENNA. RECEIVED FEBRUARY 26, 1949

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[11] J. Wust and E. Lange, *Z. physik. Chem.*, **116**, 161 (1925).

[12] F. R. Bichowsky and F. D. Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

[13] At the lowest measured concentrations Wust and Lange's curve had a slope opposite in sign to that expected from the Debye-Hückel theory. The expected reversal in slope below their lowest measured concentration was confirmed by Hammerschmid and Robinson and again by the results of the present study.