NOTES

Specific Heats of Acetaldehyde and Acetaldehyde Dibutyl Acetal

By Albert Z. Conner, Philip J. Elving[1] and Samuel Steingiser[2]

In studying the reaction

$$CH_3CHO + 2C_4H_9OH{=}CH_3CH(OC_4H_9)_2 + H_2O$$

it was necessary to know the specific heats of the compounds involved at various temperatures. Although values for water[3] and *n*-butanol[4] can be found in the literature, no values for the specific heats of liquid acetaldehyde or of acetaldehyde dibutyl acetal could be found. Accordingly, the specific heats of the latter two compounds were measured on redistilled samples of acetaldehyde (boiling at 20° at 760 mm. of mercury) and of acetaldehyde dibutyl acetal (boiling at 90° at 30 mm.); the purity of the two compounds based on physical constants and chemical analysis was not less than 99 mole per cent.

A calorimeter, similar to that described in Weissberger,[5] was employed, consisting of a silvered Dewar flask closed by a stopper through which were introduced a Beckmann thermometer, an ordinary mercury thermometer, a propeller stirrer, and a manganin coil heater. The calorimeter was almost completely immersed in a bath capable of maintaining the temperature within ±1° of the temperature of the calorimeter. The heat input was measured electrically as described in Weissberger,[6] and the time was measured by means of a stop watch.

The duration of the run was chosen to give approximately a one-degree rise in temperature. For ease of calculation and uniformity of conditions, two-minute runs were used in the determinations on both of the compounds. This time was of necessity increased to three minutes when water was used in the calibration of the calorimeter.

Due to the extremely small thermal head between calorimeter and bath, the conduction, convection and radiation losses were assumed to be negligible. In order, however, to correct for possible evaporation losses and to determine which portion of the heat input was utilized in the resultant temperature rise, a plot of calorimeter temperature *versus* time was made for each run. The corrected temperature rise was then obtained by the linear extrapolation of the temperature observations which constituted the "fore" and "after" periods, to the time when the temperature of the calorimeter was equal to the average of the values at the start and finish of the reaction period.[7]

The average values of the specific heats obtained by the method described are as follows

Compound	Temp., °C.	Specific heat, C_p cal./g.-degree
Acetaldehyde	0	0.522 ± 0.004
Acetaldehyde dibutyl acetal	25	.483 ± .004
	40	.484 ± .004
	60	.498 ± .005
	80	.513 ± .005

Publicker Industries, Inc.
Philadelphia, Pa.
Received February 1, 1947

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[3] N. H. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 238 (1939).

[4] E. W. Washburn, ed., "International Critical Tables," Vol. 5, McGraw-Hill Co., New York, N. Y., 1929, p. 108.

[5] A. Weissberger, ed., "Physical Methods of Organic Chemistry," Vol. 1, Interscience Publishing Co., New York, N. Y., 1945, p. 365.

[6] Ref. 3, p. 330–332.

[7] Ref. 3, pp. 337–340.

Recognition of Solid Solutions

By J. G. Aston, M. R. Cines and H. L. Fink

It has not generally been recognized that a complication of solid solution formation during determination of the amount of impurity by a study of melting point can frequently be detected from calorimetric melting point data on a single sample of a compound.

In the evaluation of the purity of samples used in calorimetric third law studies, Johnston and Giauque[1] pointed out that there were two ways in which the impurity might be determined. First, it is possible to determine purity from the melting point depression. Second, purity may be calculated from "premelting heat capacity." When the impurity is ideally liquid-soluble and solid-insoluble, the results of calculation by the two methods should agree. In fact, when the amount of impurity calculated from melting point depressions and from premelting heat capacities agree it may be considered as sufficient proof of the ideality of the solutions and the solid insolubility of the impurity.

A consideration of the shape of the heat–capacity–temperature curve for an ideal homogeneous solid solution near the fusion region shows that the heat capacity will break sharply at the beginning of fusion (solidus point) rather than gradually increase as in the case where no solid solution forms and the composition is far removed from that of the eutectic. Therefore, when solid solutions are studied calorimetrically in the fusion region, it will be found that the mole per cent. of impurity calculated from "premelting" heat ca-

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[1] Johnston and Giauque, This Journal, **51**, 3194 (1929).

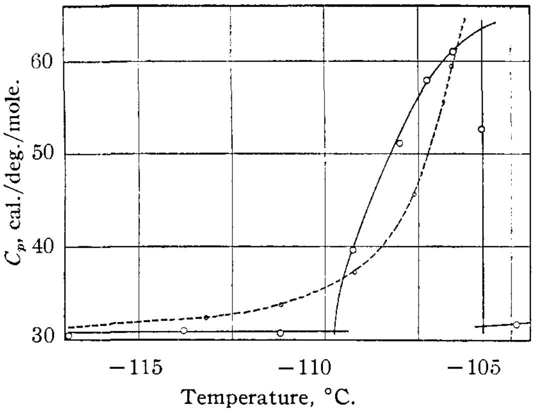

Fig. 1.—Heat capacity of 2,2-dimethylbutane with 4.6 mole per cent. 2,3-dimethylbutane added.

pacities will be much less than those found by melting point depression.

As an example of the behavior of a solid solution, the following results were obtained from the calorimetric data obtained on a mixture of 95.4 mole per cent. 2,2-dimethylbutane and 4.6 mole per cent. 2,3-dimethylbutane (a system known to form solid solutions)[2a] in a specially designed melting point calorimeter for which an accuracy of 2–3% is claimed.[2b] The amount of 2,3-dimethylbutane in the mixture was calculated to be 0.24 mole per cent. based on the 50 and 100 per cent. melted points. It was not possible to calculate the amount of impurity from the "premelting" heat capacities as there was no "premelting" rise in the heat capacity curve but rather a sharp break indicative of solid solutions. This sharp break can be seen in Fig. 1 in which heat capacity determinations on this mixture over the temperature range where it changes completely from solid to liquid are plotted as the solid line. The dashed curve represents the "premelting" heat capacity curve which was calculated for 0.24 mole per cent. liquid-soluble solid-insoluble impurity. The dashed curve was obtained by adding to the molal heat capacity of the sample, as determined at the same time as the melting point, the excess heat capacity which would be caused by "premelting" of the sample were it to contain 0.24 mole per cent. solid-insoluble impurity.

As a second example, the following results were obtained in a calorimetric determination of the purity of a sample of butadiene-1,2. Purity calculated from the 50 and 100% melted points was 99.87 and from the premelting heat capacities was 99.95 which indicates the presence of solid soluble

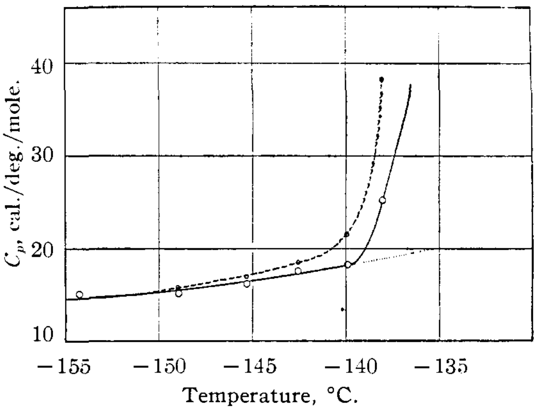

Fig. 2.—Heat capacity of butadiene-1,2.

material. The heat capacity data are plotted in Fig. 2 in which the dotted curve represents an attempted extrapolation to obtain the heat capacity curve if no premelting occurred, while the dashed curve represents the heat capacities calculated on the basis of 0.13 mole per cent. liquid-soluble solid-insoluble impurity.

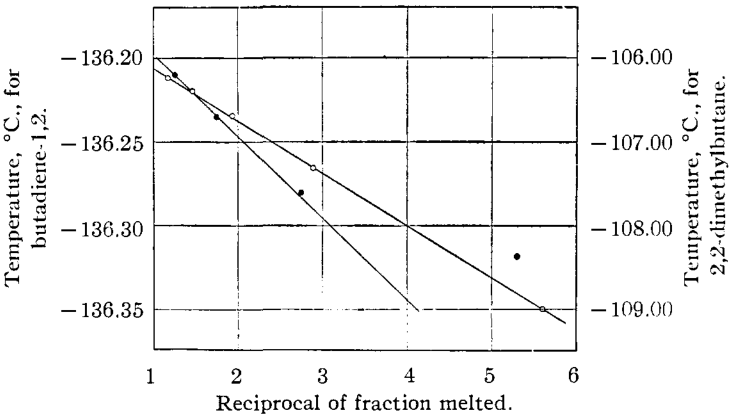

Fig. 3.—Melting curves. for butadiene-1,2 (○) and 2,2-dimethylbutane (●).

In Fig. 3 the equilibrium temperatures during melting are plotted against the reciprocal of the fractions melted. The straight lines are the theoretical curves obtained for the molar impurities as calculated from the 50 and 100% melted points; the solid points are the data for the 2,2-dimethylbutane–2,3-dimethylbutane mixture and the open circles are the data on 1,2-butadiene. It can be seen that the deviation of the points from the lines are not as spectacular as are the differences between the purities calculated from the "premelting" heat capacities and the melting point depression.

Thus, it is clear that by an examination of the "premelting" heat capacities and by a comparison with the values to be expected on the basis of the impurity determined from melting point depression it is possible by calorimetric data to reveal the existence of solid-soluble impurities. We

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(2) (a) Fink, Cines, Frey and Aston, THIS JOURNAL, **69**, 1501 (1947); (b) Aston, Tooke, Fink and Cines, *Ind. Eng. Chem., Anal. Ed.*, **19**, 218 (1947).

hasten to add that the foregoing statement applies only for systems containing relatively small amounts of the second component which would be likely to behave as an ideal solute because of its small concentration and chemical similarity, for example, hydrocarbons containing a small amount of a second component as impurity.

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RECEIVED NOVEMBER 20, 1946

The Resolution of Atabrine Dihydrochloride

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In a forthcoming publication Seeler and Malanga[3] describe their findings concerning the comparative activity of the optical isomers of atabrine against avian malaria. In our attempt to prepare the necessary optical isomers used in the above work, the methods of Chelintsev and Osetrova[4] were tried without marked success. As a result we investigated the use of other bromocamphorsulfonic acids and, as will be described below, found that the 3-bromo-[*d*-camphor]-sulfonic acid-7 formed diastereoisomeric salts which were easily separable.

Experimental

3-Bromo-(*d*-camphor)-sulfonic Acid-7.—This substance was prepared using the method of Kipping and Pope,[5] who described the formation of its ammonium salt. The actual free acid was prepared from the ammonium salt by the use of excess barium hydroxide to eliminate the ammonia followed by quantitative addition of 2 *N* sulfuric acid to remove the barium as sulfate. The aqueous solution of the free acid so obtained was concentrated under reduced pressure to a light yellow sirup which crystallized as a hydrate. This was subsequently dried *in vacuo* at 100° to yield the solid anhydrous acid which was not further treated before use.

The Resolution of *d,l*-Atabrine.—Eleven and four-tenths grams of atabrine base and 17.6 g. of 3-bromo-(*d*-camphor)-sulfonic acid-7 were heated on the steam-bath in 10 cc. of ethylene glycol monoethyl ether (cellosolve) until a clear thick sirup was obtained. The sirup was then dissolved in 500 cc. of hot acetone, immediately filtered and the filtrate allowed to stand at room temperature at least overnight, during which time crystallization occurred. Nine grams (fraction 1) of a partially resolved *d*-atabrine 3-bromo-(*d*-camphor)-sulfonate-7 was obtained on filtering.

In following the degree of resolution achieved in any fraction, the following procedure was developed for evaluating the specific rotation. A weighed sample of the atabrine sulfonate salt (about 20 mg.) was dissolved in about 10 cc. of water and after treatment with 2 drops of about 30% sodium hydroxide, to liberate the atabrine base, the whole was extracted with an equal volume of diethyl ether. After equilibration and washing with water, an aliquot of the ether phase (8 cc.) was removed and extracted with 3 cc. of water containing 2 drops of *N* hydrochloric acid. The ether phase was then removed and the aqueous phase freed of dissolved ether by heating on the steam-bath for a few minutes. The optical rotation of this solution was then observed in the usual manner. The atabrine dihydrochloride concentrate was determined by spectrophotometry at the 4250 Å. band head after appropriate dilution with *p*H 2 glycine-hydrochloric acid buffer. Under these conditions the specific absorption of pure atabrine dihydrochloride was $E^{1\,\mathrm{cm.}}_{1\%}$ 198, and satisfactory agreement with Beer's law was found. The specimen of *dl*-atabrine dihydrochloride used for establishing the above extinction coefficient was found by solubility analysis to be better than 99% pure. Fraction 1 was thus found to correspond to atabrine dihydrochloride of $[\alpha]^{23}\mathrm{D}$ +163° (dilute hydrochloric acid).

The 9 g. of fraction 1 was dissolved in 20 cc. of absolute ethanol, 60 cc. of acetone was added, and after seeding and standing overnight 6 g. (fraction 2) of acetone-washed material was obtained by filtration. Fraction 2 was found to correspond to a dihydrochloride of $[\alpha]^{23}\mathrm{D}$ +262° (dilute hydrochloric acid).

Fraction 2 was treated like fraction 1, using the ethanol–acetone procedure, whence 3 g. was obtained of fraction 3, corresponding to dihydrochloride $[\alpha]^{23}\mathrm{D}$ +310°. Investigation showed that it was no longer profitable to recrystallize the enriched bromocamphorsulfonate salts further, and so they were converted to the free bases by extraction of the ammoniacal solutions with ether. The ammonium 3-bromo-(*d*-camphor)-sulfonate-7 may be easily recovered from these ammoniacal mother liquors. The ether extracts of atabrine bases were treated with aqueous hydrochloric acid and on concentration of these aqueous solutions the dihydrochlorides crystallized out. In this manner fraction 3 yielded a crystalline dihydrochloride which, after drying (two hours *in vacuo* at 76°) and loss of 5.5% moisture, was found to have the following properties.

Anal. Calcd. for $C_{23}H_{30}ON_3Cl\cdot 2HCl$: C, 58.41; H, 6.82; N, 8.90. Found: C, 58.13; H, 6.73; N, 9.08. Specific rotation $[\alpha]^{23}\mathrm{D}$ +311° (5.2 g. per 100 cc. water).

Subsequent investigation revealed that the recrystallization of either *d*-enriched or *l*-enriched atabrine dihydrochloride from water always resulted in deposition of the optically inactive racemate thus concentrating the *d* or *l* isomer in the mother liquor. The use of hot absolute ethanol as the crystallization medium circumvented this. Recrystallization of the +311° fraction from absolute ethanol yielded a product having a specific rotation of $[\alpha]^{23}\mathrm{D}$ +355° (2.0 g. per 100 cc. water) and a specific absorption coefficient $E^{1\,\mathrm{cm.}}_{1\%}$ of 198 at 4250 Å. in *p*H 2.05 buffer. Chelintsev and Osetrova reported a value of +357° for the specific rotation of their pure dextro isomer. The material of $[\alpha]^{23}\mathrm{D}$ +355° was used by Seeler and Malanga in their avian malaria experiments.

The mother liquors from fraction 1 deposited, on longer standing in the ice-box (2°) and after seeding with a small sample of enriched *l*-atabrine 3-bromo-(*d*-camphor)-sulfonate-7 (these seeds were obtained during a preliminary small scale pilot experiment), 6 g. (fraction 4) of a salt corresponding to dihydrochloride of specific rotation −158°. The levo enriched fraction 4 was converted to the dihydrochloride as described above, and 1.2 g. of the pure levo isomer isolated directly by recrystallization from absolute ethanol. This product was found to have a specific rotation $[\alpha]^{23}\mathrm{D}$ of −334° (2 g. per 100 cc. water) and a specific absorption coefficient $E^{1\,\mathrm{cm.}}_{1\%}$ of 192. These values were determined on undried material. Drying for two hours at 76° *in vcauo* resulted in a weight loss of 9%.

Anal. Calcd. for $C_{23}H_{30}ON_3Cl\cdot 2HCl$: C, 58.41; H, 6.82. Found: C, 58.46; H, 7.09.

This material was also used by Seeler and Malanga in their avian malaria experiments.

Neither of the optical isomers was found by Seeler and Malanga to be more effective than the *d,l* mixture for

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[3] A. O. Seeler and C. Malanga, *Proc. Soc. Exptl. Biol.*, forthcoming publication.

[4] Chelintsev and Osetrova, *J. Gen. Chem., U. S. S. R.*, **10**, 1978 (1940); *C. A.*, **35**, 4029 (1941).

[5] F. S. Kipping and W. J. Pope, *J. Chem. Soc.*, **67**, 356 (1895).