Trimethylcarbinol as a Cryoscopic Solvent

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In seeking for a cryoscopic medium of moderate solvent power and having a melting point not far removed from room temperature trimethylcarbinol appeared to possess the desired properties. The cryoscopic constant of trimethylcarbinol as given in the "International Critical Tables" was found to be 12.80 whereas the value of K_f derived by means of the familiar formula of van't Hoff is 6.09 or 8.15 according to whether one uses the value of De Forcrand[1] for the heat of fusion, 29.29 cal./g., or the value of Parks and Anderson,[2] 21.88 cal./g. While these two values of L_f were determined by different methods, each is recorded in the "I. C. T." without comment as to which is the more dependable. As the result of a series of freezing point measurements, Atkins[3] found that the value of K_f varied from 7.29 to 15.44 with a mean value of 12.80 as cited above.

In view of these widely discordant data a redetermination of K_f was undertaken in the hope of verifying the accuracy of one of the above values. Trimethylcarbinol from Eastman Kodak Co. was subjected to prolonged dehydration over lime, after which it was fractionated. The product boiled at 82–83° (760 mm.) and melted sharply at 25.1°.

Atkins found difficulty in obtaining a sample of trimethylcarbinol the melting point of which remained constant for any appreciable period of time, notwithstanding precautions taken to overcome its marked hygroscopic character. After much experimentation he inclined to the belief that inconstancy of melting point was due to the existence of two different crystalline modifications, the less stable of which possesses the higher melting point and tends to undergo transformation into the stable form of lower melting point.

This difficulty has been obviated by removing the freshly distilled solvent to a room whose temperature was considerably lower than its freezing point, thereby preserving it in the solid state except when required for use. By this simple procedure the melting point of the solvent was found to alter only slightly with time; in fact

during an interval of more than two months the melting point underwent a lowering of less than 0.03°.

A series of thirty typical liquids, all Eastman Kodak Co. products, were used as solutes, each having been checked as to boiling point. Liquids were employed in preference to solids not only because of their greater solubility but because of the greater accuracy obtainable in weighing successive additions to the solvent by means of a weight pipet. All of the measurements were carried out with an ordinary freezing point apparatus using a Beckmann thermometer which had been certified by the Bureau of Standards. The temperature of the refrigerating bath ranged from 19 to 20° throughout the entire series of experiments while the customary precautions were taken to eliminate errors due to supercooling.

Upon the completion of each series of measurements with a particular solute large-scale diagrams were plotted of the observed freezing points *versus* the corresponding values of concentration and from the smoothed curves thus obtained the freezing points at even concentrations were read off and tabulated. The slope of each curve at the origin served as a measure of the cryoscopic constant, K_f. The values of K_f thus determined were found to show a greater variation than might reasonably be ascribed to the accumulated experimental errors. This departure from constancy was attributed to possible association between the molecules of solute and solvent, a view which has been strengthened by the results of subsequent molecular weight determinations in trimethylcarbinol. After making due allowance for experimental errors and in consideration of hitherto established associative tendencies of certain of the solutes, the experimental data have been classified as "Normal" and "Abnormal" as shown in Table I.

As will be noted, the mean value of K_f from the foregoing data is 8.37, whereas the value computed from the value of the heat of fusion, as determined by Parks and Anderson, is 8.15. Indirectly, the above result indicates that the value of L_f as determined by De Forcrand is erroneous. It should also be pointed out that

(1) De Forcrand, *Compt. rend.* **136**, 1034 (1903).

(2) Parks and Anderson, THIS JOURNAL, **48**, 1508 (1926).

(3) Atkins, *J. Chem. Soc.*, **99**, 10 (1911).

TABLE I

Solute	K_f (normal)	K_f (abnormal)
Water	..	9.05
Ethyl alcohol	..	8.78
Benzene	8.50	..
Formamide	..	9.20
1,4-Dioxane	8.50	..
Ethyl acetate	..	8.55
Triethylamine	..	8.60
Mesityl oxide	..	9.17
Acetonitrile	8.24	..
Cyclohexane	8.20	..
Carbon tetrachloride	8.40	..
n-Butyl ether	..	8.70
Benzyl alcohol	..	9.44
Aniline	8.20	..
Allyl alcohol	8.48	..
Pyridine	..	8.80
Anisole	8.40	..
Phenetole	8.50	..
Phenyl acetate	..	8.60
Ethyl iodide	..	7.84
n-Propyl ether	..	8.60
n-Amyl ether	..	8.72
Isopropyl ether	8.40	..
Methyl acetate	8.42	..
n-Propyl acetate	..	9.17
n-Butyl acetate	..	8.93
Amyl acetate	..	9.11
Acetone	8.20	..
Nitrobenzene	8.45	..
Nitromethane	8.29	..
Mean	8.37	

among those substances for which K_f was found to be abnormal are a number of compounds which have long been regarded as exhibiting associative tendencies. In this connection it may be mentioned that in an experimental study of mixtures of trimethylcarbinol and water Paternò[4] showed that the two components combine to form the compound $(CH_3)_3COH \cdot 2H_2O$, although subsequent viscosity studies have indicated that the above hydrate is completely dissociated at a temperature only a few degrees above the melting point of the alcohol.

In Table II the molecular weight data obtained with three substances previously studied by Atkins are summarized briefly.

The results obtained by Atkins with these substances may be summarized as follows: with p-toluidine the values of M ranged from 61.7 to 65.8 between 0.027 and 0.326 molar concentration, with α-naphthylamine M varied from 108.6 to 152.2 between 0.031 and 0.671 molar concentration, while with acetanilide M ranged from 75

(4) Paternò, Atti. Accad. Lincei, [V] 16, II, 153 (1907).

TABLE II

m	Δt	M
	p-Toluidine ($M = 107.1$)	
0.05	0.424	105.7
.10	.840	106.7
.15	1.260	106.7
.20	1.680	106.7
.25	2.104	106.5
.30	2.524	106.5
.35	2.946	106.5
	α-Naphthylamine ($M = 143.1$)	
0.05	0.500	119.8
.10	.976	122.8
.15	1.420	126.6
.20	1.816	131.9
.25	2.194	136.6
.30	2.546	141.1
	Acetanilide ($M = 135.1$)	
0.05	0.550	102.8
.10	1.044	108.2

to 156 between 0.038 and 0.631 molar concentration.

Here again there is distinct evidence of associative action as the concentration of the solution is increased. The lack of agreement between the two sets of measurements may reasonably be ascribed to the difference in the method of preservation of the solvent as already outlined.

With due care in the preparation and preservation of the solvent as herein described, trimethylcarbinol has been found to be an entirely satisfactory cryoscopic solvent, particularly where a solvent is desired whose melting point is not far removed from room temperature.

Summary

The cryoscopic constant of trimethylcarbinol has been determined by means of a series of freezing point measurements and found to be 8.37. The heat of fusion of trimethylcarbinol as determined by Parks and Anderson is 21.88 cal./g., whereas the value of this constant as calculated by means of the familiar van't Hoff equation, making use of the experimentally determined value of $K_f = 8.37$, is 21.3 cal./g. thereby confirming the results of Parks and Anderson. The experiments leading to the establishment of the value of the cryoscopic constant together with subsequent molecular weight determinations reveal a marked tendency toward both solute and solution association.