Solid–Liquid Phase Diagram of the System Methanol–Water

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The melting points of methanol–water solutions were determined from warming curves in the region above 50 mole per cent methanol. The eutectic is placed at $-116.2°$ C. and 80.3 mole per cent methanol. Using an ultrasimplified model to account for the nonideality of the solutions, it is estimated that the compound, $CH_3OH \cdot H_2O$ (s), which undergoes a peritectic decomposition at $-102.2°$ C., has a heat of fusion of 2080 ± 200 cal./mole.

A SOLUTION of methanol and water that is methanol-rich tends to form a glass when cooled below the melting point. The liquid is very viscous at such temperatures (below $-100°$ C.) because of the presence of hydrogen-bonded polymers. Because it is difficult to induce crystallization, the melting point is determined from a warming curve. Much of the wide divergence of melting point data for the composition range of 55 to 95 mole per cent methanol (1, 2, 4, 8) results from the use of cooling curves. Vuillard and Sanchez (11) appear to be the first to use warming curves throughout this region. From their results it is possible to construct the melting point curve with greater assurance than before. Also, it is reasonably certain that the compound $CH_3OH \cdot H_2O(s)$ exists since the invariant eutectic transformation has been traced to 50 mole per cent methanol. Nevertheless not enough data is reported to place the eutectic liquid composition with certainty or to permit a thermodynamic analysis of these solutions. Below 55 mole per cent methanol, where ice is the solid phase, the melting point curve has been fairly well established (1, 7, 8, 9, 11).

An accurate determination of the excess thermodynamic functions of these interesting solutions requires precise calorimetric data but such data are not yet forthcoming, and it was felt that additional measurements with a simple, conventional melting point apparatus could contribute to such future studies. Accordingly, the melting point curve in the methanol-rich region was redetermined. The complete solid-liquid phase diagram, based partially on our results, is shown in Figure 1. There remains the remote possibility of solid solution formation. It would be difficult to separate any of the solid phases from the viscous solutions with which they are in equilibrium. On the assumption that the present diagram is correct in this respect, activity coefficients were calculated and the heat of fusion of the 1:1 compound was estimated.

EXPERIMENTAL

Warming curves were obtained for 18 solutions of methanol and water ranging in composition from 54 to 95 mole per cent methanol. The solution samples were contained in a cylindrical, double-walled vessel of borosilicate glass, which was 10 cm. deep and had a capacity of 60 cc. The vessel was fitted through a $^3\frac{4}{4}_5$ standard taper joint with a cap, which provided a tight fitting sleeve for the stirrer, a thermocouple well, and a port for introducing ground glass. The temperature of the sample in the cell was measured with a copper-constantan thermocouple which had been calibrated at the dry ice point by the procedure of Scott (10). Good thermal contact between the thermocouple and the solution was assured by filling the lower portion of the well with n-pentane.

To commence a run, the cell was filled with about 40 cc. of solution and immersed in liquid nitrogen. When the temperature of the sample was 10 to 20° C. below the melting point, crystallization of the supercooled mass was induced by adding a pinch of ground glass. The cell jacket was evacuated at this juncture through a high vacuum pumping system, and the liquid nitrogen bath was replaced with a frozen slush of C. P. methanol. The rate of warming was always slow enough (about 0.4° C. per minute for the completely melted sample) to give a well defined break at the initial freezing point. The solution was constantly stirred during the run.

A reproducibility of $\pm 0.1°$ C. was obtained from the warming curves. As expected, cooling curves gave unreliable results. At compositions close to the eutectic, however, it was possible to measure the eutectic invariant temperature from both cooling and warming curves. The cooling curves gave results which were 1° C. lower, indicating that the results from warming curves could be perhaps 0.5° C. high. Except as an indication of the maximum limit of error in our measurements cooling curve results have been disregarded since freezing occurred on the walls of the cell during cooling, whereas the solid phase remained well dispersed throughout the solution during warming, and the eutectic represented the most unfavorable conditions
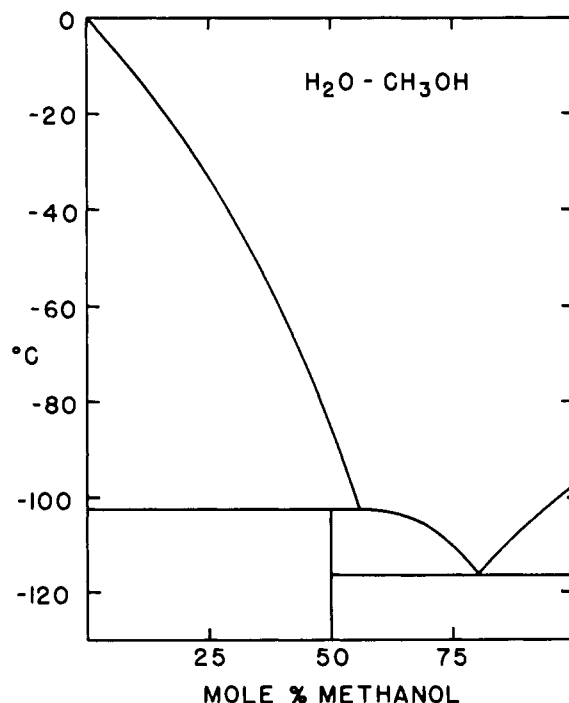

Figure 1. Solid-Liquid phase diagram of methanol–water

encountered and at temperatures only a few degrees higher, solutions were notably less viscous.

The solutions were made up by weight from distilled water and reagent grade anhydrous methanol. Contact with the atmosphere was kept at a minimum during transfer of the solutions. The cooled solutions were sufficiently protected from atmospheric moisture, since runs made on the same sample produced no observable drift in the melting point.

RESULTS AND CALCULATIONS

The data obtained from the warming curves are given in Table I and compared with the data of previous workers in Figure 2. The eutectic transition occurred at $-116.2°$ C.; the eutectic composition was 80.3 mole per cent methanol. In general, our results agree with those of Vuillard and Sanchez (11) who obtained a eutectic of $117.4°$ C., and 82 mole per cent methanol. However, they reported fewer data points in this region of the phase diagram. Pure, solid methanol is known to undergo a transition at $-115.8°$ C., involving only 153 cal./mole (3). This is very close to the eutectic temperature and could not be detected in any of the runs.
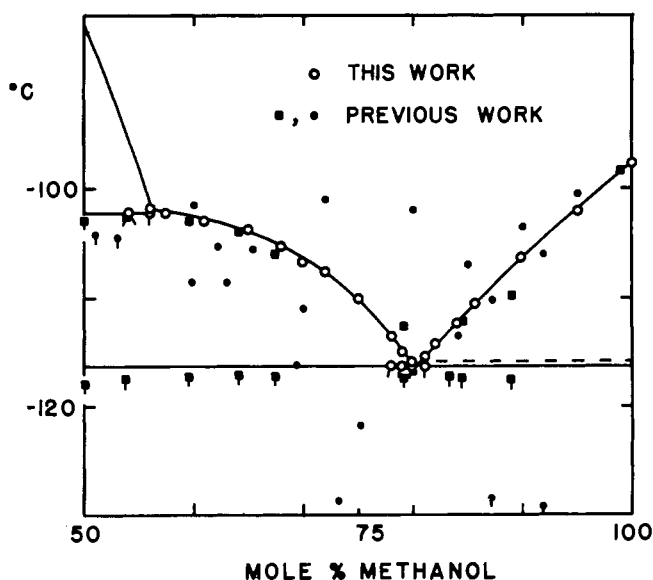

Figure 2. A portion of the solid-liquid phase diagram of methanol–water. Solid squares are data of Vuillard and Sanchez (11). Data points with tails are invariant temperatures. Dashed line is undetected transition in solid methanol

With our data on the freezing point lowering of methanol by water, we have calculated activity coefficients of methanol (Table II) from the approximate relation:

$$\ln\left(\frac{1}{\gamma_2 X_2}\right) = \frac{\Delta H - \Delta C_p T_0}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) + \frac{\Delta C_p}{R}\ln\left(\frac{T_0}{T}\right) \quad (1)$$

where the terms ΔH and ΔC_p are the values for the pure solvent at its melting point, T_0. The values used were $T_0 = 175.6°$ K., $\Delta H = 765.5$ cal./mole, and $\Delta C_p = 4.48$ cal./mole ° C. (3).

Equation 1 was applied to the freezing point lowering of water by methanol to obtain activity coefficients of water (Table III). For this purpose the previously reported melting point data for this region of composition were smoothed. The values of the terms refering to the solvent water were $T_0 = 273.2°$ K., $\Delta H = 1436$ cal./mole and $\Delta C_p = 9.0$ cal./mole ° C. (5). Because of the large temperature range involved in this latter calculation, the activity coefficients must be considered tentative. However, it is clear that the deviation from ideality is negative and rather large.

The complexity of solutions of methanol and water rather precludes finding a realistic, and at the same time workable, model to represent them. We find, nevertheless, that an ultrasimplified model corresponds reasonably well to our calculated values of the activity coefficients. This leads us to approximate values for the activity coefficients of those solutions which can be in equilibrium with the compound, $CH_3OH \cdot H_2O(s)$. The first assumption is that the only species in a solution of methanol and water are methanol monomers, water monomers, and the mixed dimer, $CH_3OH \cdot H_2O$. If X_1 and X_2 are the stoichiometric mole fractions of water and methanol, respectively, the mole fraction of the mixed dimer is given by either of two equations:

$$x_{12} = \frac{X_1 - x_1}{X_2}, \quad x_1 = \text{mole fraction of } H_2O \text{ monomer}$$

$$x_{12} = \frac{X_2 - x_2}{X_1}, \quad x_2 = \text{mole fraction of } CH_3OH \text{ monomer}$$

If we state further that the solution is ideal with respect to the three assumed species, then

$$x_1 = \gamma_1 X_1$$
$$x_2 = \gamma_2 X_2$$

Values of the equilibrium constant for mixed dimerization

$$K = \frac{x_{12}}{x_1 x_2}$$

Table I. Results of Warming-Curves for Methanol–Water Solutions

Mole % CH$_3$OH	M. P., ° C.	Plateau, ° C.
54.1		-102.2
56.0	-101.9	-102.2
57.4	-102.3	
60.9	-102.9	
65.0	-103.7	
68.0	-105.3	
69.9	-106.7	
72.0	-107.6	
75.2	-110.1	
78.0	-113.5	-116.2
79.0	-114.9	-116.3
79.9	-115.9	-116.2
81.1	-115.4	-116.3
82.0	-114.1	
84.0	-112.3	
85.6	-110.5	
89.8	-106.3	
95.0	-102.0	

Table II. Activity Coefficients of Methanol in Methanol–Water Solutions

° C.	Mole % CH$_3$OH	γ(CH$_3$OH)
-102.0	95.0	0.995
-106.3	89.8	0.995
-110.5	85.6	0.988
-112.3	84.0	0.985
-114.1	82.0	0.981
-115.4	81.1	0.976

Table III. Activity Coefficients of Water in Methanol–Water Solutions

° C.	Mole % H$_2$O	γ(H$_2$O)
-20	84.0	0.976
-40	72.5	0.926
-60	61.4	0.900
-80	51.9	0.870
-100	44.6	0.839

which satisfy the activity coefficients in Tables II and III are surprisingly independent of temperature and composition (Table IV). We choose as an average value, $K = 1$, which yields the relation

$$x_{12} = \frac{(1 - X_1 X_2) - (1 - 2 X_1 X_2)^{1/2}}{X_1 X_2}$$

The melting of the 1:1 compound may be divided thermodynamically into two steps

$$CH_3OH \cdot H_2O(s) \rightarrow CH_3OH \cdot H_2O(soln.) \rightleftharpoons$$

$$CH_3OH(soln.) + H_2O(soln.)$$
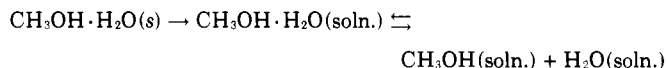
of which the second has an almost zero heat effect because of the near constancy of K. The heat of fusion, then, is given by the relation

$$\frac{d \ln x_{12}}{d\, 1/T} = \frac{\Delta H}{R}$$

A plot of $\ln x_{12}$ vs. $1/T$ using our eleven data points between the peritectic and eutectic yields the value, $\Delta H = 2080 \pm 200$ cal./mole.

An indication of the sensitivity of the derived heat of fusion to the choice of a model may be had by comparison with the result based on une assumption that the solutions are ideal. The relevant equation in this case is

$$\frac{d \ln X_1 X_2}{d\, 1/T} = \frac{\Delta H}{R}$$

which yields a value of about 1600 cal./mole for the heat of fusion of the 1:1 compound.

Our model is, of course, an unrealistic picture of the hydrogen bonded polymerization that takes place in a solution of water and methanol, and in particular cannot account for the positive deviations from Raoult's law that such solutions show at higher temperatures (6). Apparently, at higher temperatures, mixed dimers play a less important role than do dimers and polymers of the respective pure components.

NOMENCLATURE

C_p = molar heat capacity at constant pressure.
H = molar enthalpy.
K = equilibrium constant.
R = gas constant, 1.98726 cal./mole ° K.
T = absolute temperature.
X, x = mole fraction.
γ = activity coefficient.

Table IV. Equilibrium Constants for Formation of Mixed Dimers in Hypothetical Model of Methanol–Water Solutions

Solid Phase	° C.	Exptl. Mole % CH₃OH	K	Calcd. Mole % CH₃OH, K = 1
Ice	−20	16.0	2.77	16.6
Ice	−40	27.5	2.20	29.0
Ice	−60	38.6	1.02	38.5
Ice	−80	48.1	0.77	46.9
Ice	−100	55.4	0.70	53.5
Methanol	−115.4	81.1	1.30	81.1
Methanol	−114.1	82.0	1.03	82.0
Methanol	−112.3	84.0	0.94	84.0
Methanol	−110.5	85.6	1.14	85.6
Methanol	−106.3	89.8	0.65	90.0
Methanol	−102.0	95.0	. . .	94.8

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