

DETERMINATION OF HEAT CAPACITY OF WATER/ETHYLENE GLYCOL MIXTURES AS A FUNCTION OF MOLE FRACTION OF ETHYLENE GLYCOL BY MEANS OF A DROP HEAT-CAPACITY CALORIMETER

A. A. Oshodi

Department of Chemistry, Federal University of Technology, Akure, Nigeria

(Received April 3, 1988; revised December 28, 1988)

The heat capacities of water/ethylene glycol mixtures were determined at 25° using the precise drop calorimeter. It was found that the plot of molar heat capacity of ethylene glycol/water mixtures shows an inflexion at about 0.20 mole fraction of ethylene glycol. This observation is interpreted in terms of structural modification of water in the mixture. It is suggested that this structural modification of water by ethylene glycol might probably contribute to the type of variation of $-\Delta H^{\circ}$ of formation of azide complex of methemoglobin in water/ethylene glycol mixtures below this region.

Key words: Heat-capacity, Water/ethylene glycol, Drop-calorimeter.

INTRODUCTION

In any thermodynamic study involving a mixture of water and a nonaqueous solvent, it is important to consider the effect of the nonaqueous solvent on the structural stability of water [1]. For instance, the introduction of a polar solute into water is accompanied by a negative partial molar entropy and large heat capacity changes. These large entropies and large heat capacities of solution are peculiar to aqueous solutions [2-4] and are attributed to solvent ordering process in presence of solute. Nwankwo and Wadso [5] observed that there is only a marginal effect of this nature when hydrophobic groups become solvated in ethylene glycol. Liquid water has been described as being composed of monomeric water molecules and "icelike" clusters of water molecules with cavities containing n -molecules linked together by hydrogen bonds [6]. From his studies on the solubility of argon in aqueous mixtures of non-electrolytes, Ben-Naim [7] has suggested that different non-electrolytes have different effects on the structure of water, those that stabilise the structure of water only at low concentration by increasing the number of cavities in the solution e.g. monohydric alcohols, while those that destabilise the structure of water reduce the number of cavities e.g. *P*-dioxan, glucose and sucrose. Ben-Naim [1] further showed that the solubility of argon in water/ethylene glycol mixtures first decreases as a function of ethylene glycol concentration and attributed this to the destabilisation effect on the structure of water. Contrary to other systems studied, Ben-Naim [7] found that at high concentration of ethylene glycol, the curve approached a limit after passing minimum point. He suggested three possibilities:

- (i) There is likely another effect which may well be called "structural effect" and that this effect will not involve the rupture of hydrogen bonds.
- (ii) Probably the water molecule and the ethylene glycol molecule can form a sort of three dimensional network through hydrogen bonds with different cavity size and shapes.
- (iii) The insertion of gas molecules into the cavities may affect the rotational and vibrational degrees of freedom of the solvent molecules resulting into little energy change but considerable entropy change and this may be typical for highly associated liquids.

From the foregoing observations and the suggestions therein, one could infer that the effect of ethylene glycol on water structure depends on the concentration of ethylene glycol in the following way, at low concentration of ethylene glycol, the structure of water is modified to some extent while as the ethylene glycol concentration increases, this modification may stop and the existing water structure becomes more stable. Thus one will expect that the heat capacities of water/ethylene glycol mixtures will vary differently at region of low concentration of ethylene glycol where the structure of water is being modified compared with when the structure becomes more stable. The following report shows the variation of heat capacity of various mixtures of water and ethylene glycol with mole fraction of ethylene glycol.

MATERIALS AND METHOD

Glass distilled, de-ionised water was used in the calibration experiments as calibration standard and for the preparation of the aqueous mixtures. Prior to its use, the

water was reboiled to remove dissolved gases. The ethylene glycol used was obtained from British Drug House and treated as in Anusiem and Oshodi [15].

A syringe was weighed with and without ethylene glycol and the weight of ethylene glycol used in preparing a mixture was calculated from the difference in weights. The weight of water used was calculated in the same way as for ethylene glycol. The sample ampoule was filled with the mixture and tightly closed with the O-ring seal. The weight of sample was obtained by difference. The reference ampoule was empty throughout the experiments.

The heat capacity measurements were carried out by means of a drop heat-capacity calorimeter. Essentially, the calorimeter assemble consists of two main parts, a furnace for temperature equilibration of two sample ampoules and a receiving twin heat conduction microcalorimeter [8,9].

A steel ampoule containing the sample and a reference ampoule were thermostated in the furnace at a temperature t_i . Thereafter, the ampoules were dropped simultaneously into the receiving calorimeter, set at a temperature t_f . Measurements were made with the ampoules empty and then with the sample ampoule containing a known quantity of sample while the reference ampoule was empty. The quantity of heat Q_{sub} transferred by the sample is calculated from the difference of measured heat quantities. The mean heat capacity for the sample in the temperature interval t_i to t_f was obtained from Q_{sub}/t where t is equal to $t_f - t_i$.

The temperature of the furnace was kept constant to better than $\pm 2 \times 10^{-4}K$ by means of a Eurotherm proportional controller (Eurotherm Limited, Warthing, Sussex England). The temperature of the water thermostat was also kept constant to about $5 \times 10^{-4}K$ using a Eurotherm proportional controller [8]. The temperatures of the furnace and calorimeter block were measured by two different quartz thermometers using a Hewlett packard quartz probe (HP - 2850A) [8].

The ampoule designed for liquids consists of a cylinder (wall thickness 0.2mm) which can be tightly closed by an O-ring seal [8]. Both ampoules have a maximum sample volume of $0.7cm^3$. The ampoules were allowed to equilibrate in the furnace for 30 minutes. By means of lift and magnet, the ampoules could drop from the furnace into the receiving calorimeter after equilibration was attained. After the calorimetric measurements, the ampoules were transferred back to the equilibration position by the magnetic lift. For the present work, the furnace temperature was 30° while the calorimeter temperature was 20° .

Each heat capacity value in the table below is an average of at least five experiments.

RESULTS AND DISCUSSION

The relationship between the partial molar heat capacity of water and ethylene glycol can be expressed as follows:

$$\hat{C}_p = m_1 C_{p1} + m_2 C_{p2} \quad \dots \dots \dots (1)$$

Where \hat{C}_p , C_{p1} and C_{p2} are the heat capacity of the mixture, partial molar heat capacity of water and ethylene glycol respectively. We can define molar heat capacity of the mixture C_p as -

$$C_p = \frac{\hat{C}_p}{m_{tot}} = \frac{m_1}{m_{tot}} C_{p1} + \frac{m_2}{m_{tot}} C_{p2} \quad \dots \dots \dots (2)$$

where m_1 and m_2 are moles of water and ethylene glycol respectively and $m_{tot} = m_1 + m_2$

$$\begin{aligned} \text{Hence } C_p &= \left(1 - \frac{m_2}{m_{tot}}\right) C_{p1} + \frac{m_2}{m_{tot}} C_{p2} \\ &= C_{p1} - \frac{m_2}{m_{tot}} (C_{p1} - C_{p2}) \quad \dots \dots \dots (3) \end{aligned}$$

where $\frac{m_2}{m_{tot}} =$ mole fraction of ethylene glycol = $X_{E. Gly.}$

$$C_p = C_{p1} - X_{E. Gly.} (C_{p1} - C_{p2}) \quad \dots \dots \dots (4)$$

a plot of C_p versus $X_{E. Gly.}$ will give C_{p1} i.e. heat capacity of water as the intercept and the heat capacity of ethylene glycol can be calculated from the slope.

The Table shows the variation of molar heat capacity of the mixture with mole fraction of ethylene glycol, and the figure shows a plot of C_p versus $X_{E. GLY.}$ From the figure, it is observed that there is an inflexion at about 0.20 mole fraction of ethylene glycol. Bull and Breese [10] had suggested that to get true intercept for this type of curve, the first few points that show linear relationship before the inflexion point could be used. The application of this suggestion on the first five points gives the intercept to be $75.321 JK^{-1} mol^{-1}$ which is the value of molar heat capacity for pure water as explained from equation [4] above. This value is comparable with $75.285 JK^{-1} mol^{-1}$ recorded in Chemical Engineering Handbook [11]. From the slope of the curve, the specific heat capacity of pure ethylene glycol was found to be $149.087 JK^{-1} mol^{-1}$

Table 1. Molar heat capacity of various mixtures of water/ethylene glycol.

Mole fraction of ethylene glycol (f)	Molar heat capacity of mixtures (C_p) ($\text{JK}^{-1} \text{mol}^{-1}$)
0.020	75.494 ± 0.014
0.030	75.693 ± 0.012
0.040	76.120 ± 0.013
0.060	79.529 ± 0.014
0.078	82.937 ± 0.015
0.124	86.578 ± 0.012
0.176	90.348 ± 0.016
0.243	94.035 ± 0.014
0.324	99.477 ± 0.018
0.421	106.159 ± 0.021
0.548	115.763 ± 0.015
0.718	127.463 ± 0.019
0.811	135.625 ± 0.018

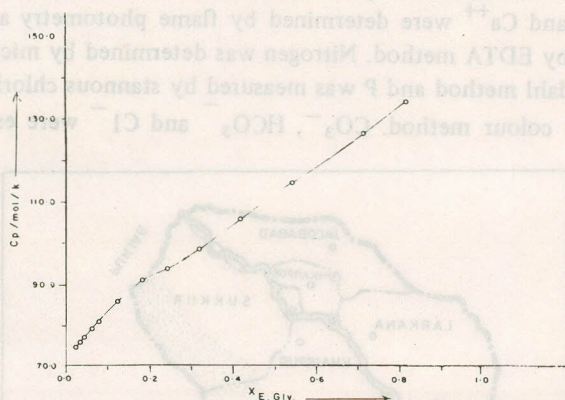


Fig. 1. Determination of heat capacity of water/ethylene glycol mixtures as a function of mole fraction of ethylene glycol by means of a drop heat capacity calorimeter.

compared with $149.336 \text{ JK}^{-1} \text{ mol}^{-1}$ obtained by Stephens and Tamplin [12] and $148.777 \text{ JK}^{-1} \text{ mol}^{-1}$ recorded in Chemical Engineering Handbook [11].

The inflexion point at about 0.20 mole fraction of ethylene glycol in the figure is similar to that observed by Nakanishi [13] and Moranas and Douheret [14] in this region for ethylene glycol/water mixture in their studies of variation of partial molar volume of some alcohols with their mole fractions. These authors suggest that this curvature may arise from the hydrogen bond formation between water and the polar group of the ethylene glycol molecule and the structural modification of the water

around these molecules. This structural modification in ethylene glycol/water mixtures has also been suggested by Ben-Naim [7] which he termed "structural effect". The heat capacity behaviour of ethylene glycol/water mixture at about 0.20 mole fraction of ethylene glycol may be due to this structural effect. Thus the observed inflexion may be due to change from the changing structure of water at low concentration of ethylene glycol to a condition where the structure of water has become more stable at higher concentration of ethylene glycol as suggested by Anusiem and Oshodi [15]. This observation may also be compared with that of Nwanko and Wadso [16] who suggested that their result may be considered as indication of reduction of the "water character" of the solvent mixture. This structural modification of water by ethylene glycol probably contributes to the type of variation of $-\Delta H^{\circ}$ of formation of azide complex of methemoglobin in this region as earlier suggested [15].

Acknowledgement. I wish to acknowledge the financial support in form of fellowship from International Seminar in Chemistry, of University of Uppsala, Sweden.

REFERENCES

1. A.J. Ben-Naim, *Phys. Chem.*, **72**, 2998 (1968).
2. H.S. Frank and Evans, *J. Chem. Phys.*, **13**, 507 (1945).
3. H.L. Scheraga, G. Nemethy and I.Z. Steinberg, *J. Boil. Chem.*, **237**, 2506 (1962).
4. K.W. Miller and J.H. Hilderbrand, *J. Amer. Chem. Soc.*, **90**, 3001 (1968).
5. S. Nwanko and I. Wadso, *J. Chem. Thermodynamics*, **12**, 881 (1980).
6. A. Ben-Naim, *J. Phys. Chem.*, **65**, 1922 (1965).
7. A. Ben-Naim, *J. Phys. Chem.*, **69**, 3245 (1965).
8. J. Suurkuush and I. Wadso, *J. Chem. Thermodynamics*, **6**, 667 (1974).
9. I. Wadso *Science Tools, the LKB Instrument J.* **21**, 18 (1974).
10. H.B. Bull, K. Breese, *Arch. Biochem. Biophys.*, **123**, 497 (1968).
11. R.H. Perry and Chilton, *Chemical Engineering Handbook*, 3-127 (1973), 5th ed.
12. M.A. Stephens and W.S. Templin, *J. Chem. and Eng. Data*, **24**, 81 (1979).
13. K. Nakanishi, *Bull. Chem. Soc., Japan*, **33**, 793 (1960).
14. M. Moranas and G. Douheret, *Thermochemica Acta*, **25**, 217 (1978).
15. A.C.I. Anusiem and A.A. Oshodi, *Arch. Biochem. Biophys.*, **189**, 392 (1978).
16. S. Nwanko and I. Wadso, *J. Chem. Thermodynamics*, **12**, 1167 (1980).