Thermochimica Acta, 103 (1986) 291–295
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

EXCESS ENTHALPY IN THE METHANOL–WATER SYSTEM AT 278.15, 298.15 AND 323.15 K UNDER PRESSURES OF 0.1, 20 AND 39 MPa. III. THE INFLUENCE OF PRESSURE ON THE EXCESS ENTHALPY

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(Received 12 December 1985)

ABSTRACT

Results of calculations of $\Delta^{p}_{0.1\text{MPa}}\ H^{\text{E}}_{T}(x)$ on the basis of experimental results reported previously are presented. The obtained results are compared with the data obtained from volumetric measurements, available from the literature.

INTRODUCTION

In previous papers [1,2] a description of experimental procedure has been given and results of measurements with the use of these procedures of excess enthalpy in the methanol–water system in the temperature range of 278.15–323.15 K and under pressures of 0.1, 20 and 39 MPa have been presented. The influence of temperature on the excess enthalpy under given pressures was emphasized. In this paper the influence of pressure is analysed in detail.

METHOD AND RESULTS

In order to distinguish the influence of pressure on the excess enthalpy from other effects the differences $\Delta^{p}_{0.1\text{MPa}}\ H^{\text{E}}_{T}(x)$ have been calculated between the excess enthalpy under a given pressure and the excess enthalpy under normal pressure (0.1 MPa)

$$\Delta^{p}_{0.1\text{MPa}} H^{\text{E}}_{T}(x) = H^{\text{E}}_{T,p}(x) - H^{\text{E}}_{T,0.1\text{MPa}}(x) \qquad (1)$$

where x is the mole fraction of methanol. The subtraction of direct experi-

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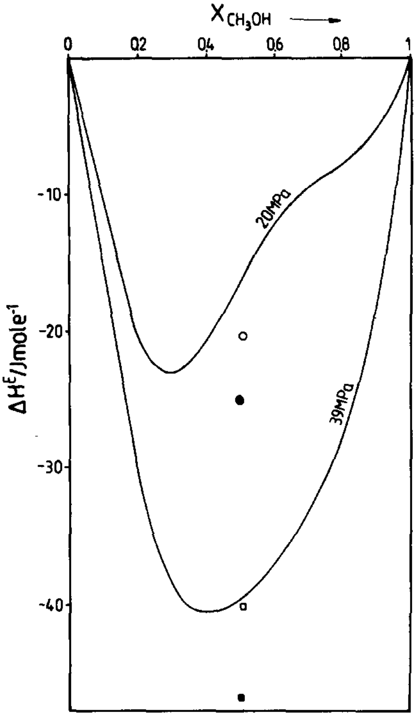

Fig. 1. Effect of pressure on the excess enthalpy in the methanol–water system at temperature 278.15 K; ○, □—results of Götze and Schneider [3], ●, ■—results of Easteal and Woolf [4].

mental data was difficult because the concentrations at which the measurements have been performed at particular pressures were different. So, the subtraction was made with the use of the analytical presentation of the results with the use of NRTL formula as described in a preceding paper [2]. The results of such calculations at temperatures 278.15, 298.15 and 323.15 K are presented graphically in Figs. 1, 2 and 3. In these figures values of $\Delta^p_{0.1\mathrm{MPa}} H^E_T(0.5)$ calculated with the use of the following formula are also presented

$$\Delta^p_{0.1\mathrm{MPa}} H^E_T(x) = \int_{0.1\mathrm{MPa}}^{p} V^E_x \mathrm{d}p - T\int_{0.1\mathrm{MPa}}^{p} \left(\frac{\partial V^E}{\partial T}\right)_{p,x} \mathrm{d}p \qquad (2)$$

The calculations are based on volumetric data of both Götze and Schneider [3] and Easteal and Woolf [4]. In the case of Götze and Schneider's data a plot of $V^E_{0.5}$ vs. temperature was made for each value of pressure and from such plots the values of both $V^E_{0.5}$ and $\left(\frac{\partial V^E}{\partial T}\right)_{p,0.5}$ at temperature 278.15 K were determined. Graphic integrations have been performed afterwards taking $V^E_{0.5}$ and $\left(\frac{\partial V^E}{\partial T}\right)_{p,0.5}$ over the pressure intervals of 0.1–20 MPa and of 0.1–39 MPa. In the case of Easteal and Woolf's data their numerical values

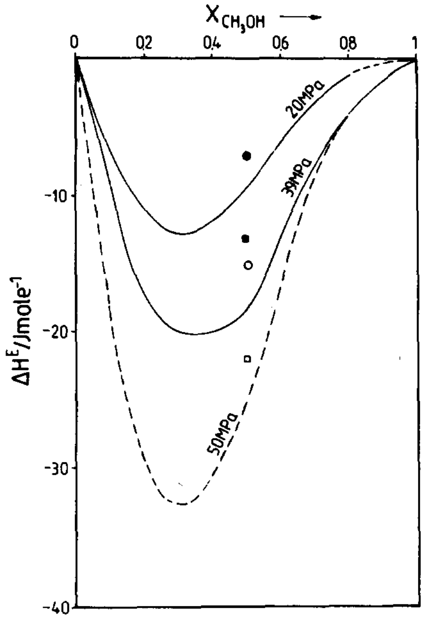

Fig. 2. Effect of pressure on the excess enthalpy in the methanol–water system at temperature 298.15 K; ○, □—results of Götze and Schneider [3], ●, ■—results of Easteal and Woolf [4], — — — — results of Heintz and Lichtenthaler [5].

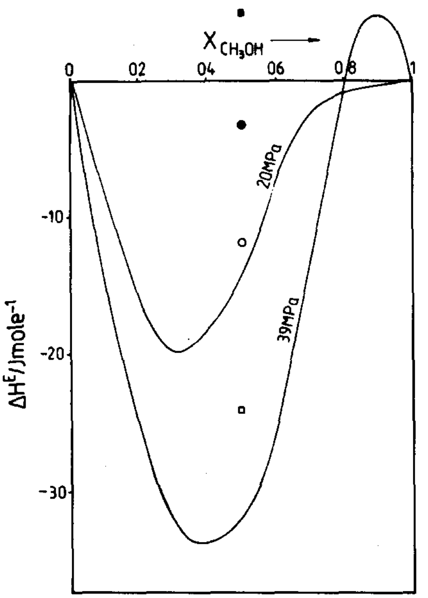

Fig. 3. Effect of pressure on the excess enthalpy in the methanol–water system at temperature 323.15 K; ○, □—results of Götze and Schneider [3], ●, ■—results of Easteal and Woolf [4].

TABLE 1

Numerical results of calculations of $\Delta^{p}_{0.1\mathrm{MPa}} H^{\mathrm{E}}_{T}(x)$ on the basis of our flow-calorimetric measurements [2] (a) and of volumetric measurements of Easteal and Wolf [4] (b) and of Götze and Schneider [3] (c)

Mole fraction of methanol	$H^{\mathrm{E}}/\mathrm{J\ mol^{-1}}$																	
	$T = 278.15$ K						$T = 298.15$ K						$T = 323.15$ K					
	$p = 20$ MPa			$p = 39$ MPa			$p = 20$ MPa			$p = 39$ MPa			$p = 20$ MPa			$p = 39$ MPa		
	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
0.1	−14	36		−18	70		−7	−9		−9	−17		−8	−6		−15	−11	
0.2	−21	4		−32	9		−11	−6		−19	−12		−16	−7		−26	−13	
0.3	−23	−11		−39	−21		−13	−8		−20	−15		−20	−13		−33	−25	
0.4	−20	−18		−41	−36		−11	−9		−20	−18		−18	−5		−34	−10	
0.5	−16	−24	−20	−39	−47	−40	−9	−7	−14	−18	−13	−22	−14	−3	−11	−32	5	
0.6	−12	−3		−36	−7		−7	−6		−13	−13		−7	−4		−25	−9	
0.7	−9	−7		−32	−14		−3	−5		−8	−10		−2	14		−14	27	
0.8	−8	−16		−28	−32		0	0		−4	−1		−1	4		3	8	
0.9	−7	−6		−20	−11		−6	−1		−1	−3		0	3		4	5	

on partial molar volumes have been recalculated to obtain V^E data. Then for each composition V^E was represented by a polynomial as a function of temperature for each value of pressure and as a function of pressure for each value of temperature. The values of derivatives $(\frac{\delta V^E}{\delta T})_{p,x}$ have been calculated by analytical differentiation and then the final integrations and summation according to formula (2) were made. Numerical data for the whole composition range are given in Table 1. One can observe that the agreement between the results taken from the three independent and different sources is satisfactory, taking into consideration that the precision of determination of $\Delta^p_{0.1\mathrm{MPa}} H^E$ is not high. For comparison $\Delta^{50\mathrm{MPa}}_{0.1\mathrm{MPa}} H^E_{298.15}(x)$ obtained by Heintz and Lichtenhalter [5] in their flow calorimeter is also presented in Fig. 2.

DISCUSSION

The increase of absolute values of $\Delta^p_{0.1\mathrm{MPa}} H^{EA}$ with pressure at the pressure range under investigation suggests that pressure stimulates the process of formation of a certain solution structure. One can assume that the reduction of the distance between molecules increases the energy of the hydrogen bond. The change of sign in our $\Delta^p_{0.1\mathrm{MPa}} H^E$ values at methanol-rich mixtures at 323.15 K under pressure of 39 MPa was presumed by us to be an effect of an overlapping of experimental and extrapolation errors. However, considering recent results of Easteal and Wolf [4], who observed a similar effect which magnitude was rising with pressure (see Table 1), one can assume that it is a result of a new phenomenon appearing in the methanol–water solution system, e.g., association of methanol. The full explanation of this phenomenon requires more experimental data at higher temperature (and possibly pressure) range.

ACKNOWLEDGEMENT

This work has been carried out within the Polish Academy of Sciences basic research program 0.3.10.1.7.2.

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