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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. II. EXPERIMENTAL RESULTS AND THEIR ANALYTICAL PRESENTATION

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ABSTRACT

Results are presented of flow-calorimetric measurements of excess enthalpy in the methanol–water system at temperatures 278.15, 298.15 and 323.15 K under pressures of 0.1, 20 and 39 MPa. The experimental results are correlated with the use of Redlich–Kister, NRTL and UNIQUAC formulas.

INTRODUCTION

In a preceding paper [1] a description was given of our flow-calorimetric system. Also the experimental procedures were presented which were used to obtain numerical data on excess enthalpy at given compositions at given pressure and temperature range. In this paper results of such measurements for the methanol–water system are presented. The experimental point data obtained from flow calorimetric measurements are correlated with the use of three known formulas (Redlich–Kister, NRTL and UNIQUAC) in order to express the excess enthalpy as a continuous function of composition at particular values of pressure and temperature. When presenting the data the influence of temperature is emphasized.

MATERIALS

Measurements have been performed with the use of carefully purified substances. The methanol samples were supplied by Chemipan ** with a gas chromatographic test of purity (less than 0.05% of impurities). The water

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samples were doubly-distilled in a quartz apparatus and then deionized. The liquid specimens were also degassed before use. The densities of the test methanol–water mixtures prepared with the materials mentioned above were almost exactly the same as those given by McGlashan and Williamson [2] and the measured deviations were less than 0.1%.

RESULTS

The results of measurements are presented in Tables 1, 2 and 3. These point data at particular values of composition have been correlated in order to obtain the excess enthalpy as a continuous function of composition at the pressure and temperature under investigation. Three different formulas have been used for the correlation:

Redlich–Kister [3]

$$H^{\mathrm{E}} = x_1 x_2 \sum_{i=0}^{n} A_i (x_1 - x_2) \tag{1}$$

NRTL [4]

$$H^{\mathrm{E}} = RTx_1x_2 \Big\{ \tau_{21}G_{21}(x_1 + x_2G_{21})^{-1} + \tau_{12}G_{12}(x_2 + x_1G_{12})^{-1} + \\ -\alpha\big[x_1\tau_{21}^2G_{21}(x_1 + x_2G_{21})^{-2} + x_2\tau_{12}^2G_{12}(x_2 + x_1G_{12})^{-2}\big]\Big\} \tag{2}$$

TABLE 1

Results of flow-calorimetric measurements of excess enthalpy in the methanol–water system under a pressure of 0.1 MPa

$T = 278.15$ K		$T = 298.15$ K		$T = 323.15$ K	
$x_{\mathrm{CH_3OH}}$	H^{E} (J mol^{-1})	$x_{\mathrm{CH_3OH}}$	H^{E} (J mol^{-1})	$x_{\mathrm{CH_3OH}}$	H^{E} (J mol^{-1})
0.110	718	0.087	510	0.065	330
0.147	839	0.131	662	0.087	404
0.179	913	0.191	782	0.089	402
0.225	962	0.250	852	0.138	540
0.237	960	0.338	870	0.180	607
0.328	974	0.357	860	0.202	635
0.358	965	0.440	825	0.214	645
0.368	950	0.525	775	0.236	663
0.467	896	0.605	702	0.247	670
0.470	912	0.672	644	0.344	702
0.510	866	0.789	465	0.350	689
0.511	868			0.440	680
0.600	786			0.446	685
0.602	778			0.535	645
				0.612	596
				0.668	543
				0.717	492
				0.784	404

TABLE 2

Results of flow-calorimetric measurements of excess enthalpy in the methanol–water system under a pressure of 20 MPa

$T = 278.15$ K		$T = 298.15$ K		$T = 323.15$ K	
x_{CH_3OH}	H^E (J mol^{-1})	x_{CH_3OH}	H^E (J mol^{-1})	x_{CH_3OH}	H^E (J mol^{-1})
0.109	730	0.104	582	0.138	551
0.178	934	0.132	677	0.141	552
0.236	982	0.144	701	0.176	616
0.358	983	0.260	863	0.180	625
0.469	918	0.352	873	0.267	701
0.512	885	0.505	799	0.269	699
0.603	791	0.602	718	0.337	716
				0.340	706
				0.435	700
				0.441	703
				0.530	660
				0.538	655
				0.600	613
				0.667	546
				0.668	547
				0.718	500

where $\tau_{12} = (g_{12} - g_{22})/RT$; $\tau_{21} = (g_{21} - g_{11})/RT$; $G_{12} = \exp(-\alpha\tau_{12})$; $G_{21} = \exp(-\alpha\tau_{21})$. So, effectively, there are three parameters in this formula to be adapted: $(g_{12} - g_{22})$, $(g_{21} - g_{11})$ and α.

UNIQUAC [5]

$$H^E = \frac{-R}{T^2}\left[-q_1x_1 \ln(\theta_1 + \theta_2\tau_{21}) - q_2x_2 \ln(\theta_2 + \theta_1\tau_{12}) + x_1 \ln\frac{\phi_1}{x_1} + x_2 \ln\frac{\phi_2}{x_2} + \frac{Z}{2}\left(q_1x_1 \ln\frac{\theta_1}{\phi_2} + q_2x_2 \ln\frac{\theta_2}{\phi_2} + q_1x_1\frac{\theta_2\tau_{21}}{\theta_1 + \theta_2\tau_{21}}(-\ln \tau_{21}) + q_2x_2\frac{\theta_2\tau_{12}(-\ln \tau_{12})}{\theta_2 + \theta_1\tau_{12}}\right]\tag{3}$$

where

$$\phi_1 = \frac{r_ix_i}{\sum_{k=1}^{2} r_kx_k}$$

$$\theta_i = \frac{q_ix_i}{\sum_{k=1}^{2} q_kx_k}$$

$$\tau_{ij} = \exp\left(-\frac{u_{ij} - u_{ji}}{RT}\right)$$

TABLE 3

Results of flow-calorimetric measurements of excess enthalpy in the methanol–water system under a pressure of 39 MPa

$T = 278.15$ K		$T = 298.15$ K		$T = 323.15$ K	
x_{CH_3OH}	H^E (J mol^{-1})	x_{CH_3OH}	H^E (J mol^{-1})	x_{CH_3OH}	H^E (J mol^{-1})
0.110	741	0.098	564	0.081	398
0.177	935	0.191	795	0.185	632
0.226	991	0.252	869	0.235	694
0.366	998	0.339	892	0.236	690
0.470	945	0.440	849	0.264	713
0.511	898	0.520	787	0.342	730
0.602	818	0.604	726	0.367	738
				0.434	713
				0.448	704
				0.614	622

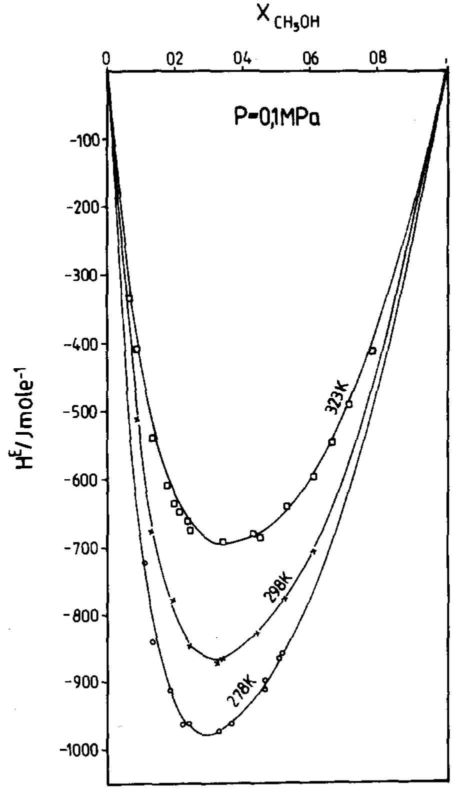

Fig. 1. Effect of temperature on the excess enthalpy in the methanol–water system under a pressure of 0.1 MPa, ○, □, × —experimental points, ——— correlation with the NRTL formula.

$z = 10$, $q_1 = 1.432$, $q_2 = 1.400$, $r_1 = 1.4311$, $r_2 = 0.920$ [6], where subscript 1 is for methanol, subscript 2 is for water. Thus in this equation there are two parameters to be adapted: $(u_{12} - u_{22})$ and $(u_{21} - u_{12})$.

The equations given above have been used in computer programs in which the sum of square deviations between the experimental values and the calculated values was minimized by the least-squares fitting procedure. The values of parameters obtained from the least square fitting procedure with the use of the particular formulas are listed in Table 4. Also given are mean square deviations between the experimental values and those calculated from formulas (1–3). The deviations were calculated from the following formula

$$SQ = \left[(n-k)^{-1} \sum_{i=1}^{n} \left(H_{i\mathrm{exp}}^{\mathrm{E}} - H_{i\mathrm{cal}}^{\mathrm{E}} \right)^2 \right]^{0.5} \tag{4}$$

where n is the number of experimental points and k is the number of parameters. It can be seen that the best presentation of experimental data is obtained with the use of NRTL formula. In Figs. 1–3 are presented both the

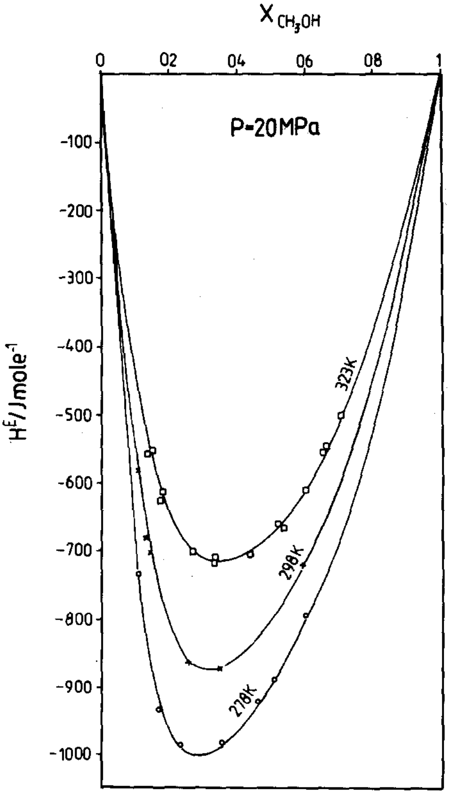

Fig. 2. Effect of temperature on the excess enthalpy in the methanol–water system under a pressure of 20 MPa, ○, □, × —experimental points, ———correlations with the NRTL formula.

TABLE 4

Parameter values for four equations used for correlation of experimental data, R–K-3 and R–K-4 are symbols for Redlich–Kister formula with three and four parameters, respectively (the parameter values for the NRTL formula are given in the following order: $(g_{12} - g_{22})$, $(g_{21} - g_{11})$, α and for the UNIQUAC formula in the following order: $(u_{12} - u_{22})$, $(u_{21} - u_{11})$, where 1 means methanol and 2 means water; SQ is the mean square deviation calculated from formula (4))

T (K)	p (MPa)	Coefficient values (J mol^{-1})				Mean sq. dev. – SQ (J mol^{-1})			
		R–K-3	R–K-4	NRTL	UNIQUAC	R–K-3	R–K-4	NRTL	UNIQUAC
278.15	0.1	−3439	−3502	23612	−2595				
		1440	1545	7930	1620	15	7	2	50
		−4140	−2491	0.256					
			2418						
278.15	20	−3499	−3566	23390	−2607				
		1513	1645	5587	1615	17	7	1	25
		−4483	−2510	0.260					
			2422						
278.15	39	−3597	−3656	15225	−2645				
		1504	1615	17045	2005	15	7	2.7	28
		−4483	−2537	0.447					
			2346						
298.15	0.1	−3102	−3170	27600	−3373				
		1755	1336	7361	−3206	18	5	0.4	2
		−2551	−2003	0.254					

298.15	20	−3156 1285 −3272	1385 −3210 1381 −1965	23988 6830 0.287	−2754 −61335	8	4	0.2	6
298.15	39	−3196 1770 2443	1448 −3241 1414 −1984	59929 5093 0.345	−2632 −51480	15	7	5	9
323.15	0.1	−2537 1194 −2176	1351 −2640 826 −1419	20092 8307 0.306	−3808 −2000	13	4	0.9	2
323.15	20	−2647 1163 −2041	1410 −2694 943 −1409	16443 8625 0.324	−4018 −1703	11	4	0.7	1
323.15	39	−2705 827 −2651	1310 −2769 909 −1355 1434	6487 7089 0.320	−2356 954	10	6	0.7	20

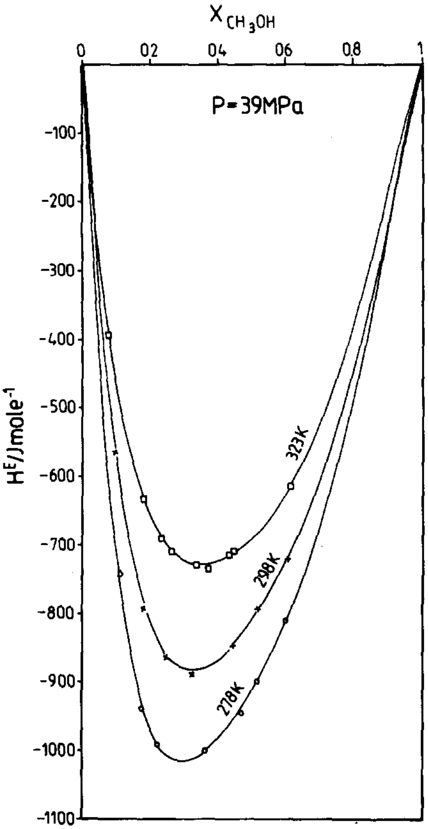

Fig. 3. Effect of temperature on the excess enthalpy in the methanol–water system under a pressure of 39 MPa, ○, □, ×—experimental points, ————correlation with the NRTL formula.

experimental values (points) and values calculated with the use of NRTL formula.

DISCUSSION

From Figs. 1–3 and the numerical presentation of the results in Tables 1–3 one can see that the absolute values of the excess enthalpy in the pressure range under investigation decrease with temperature. At the same time the extremum is shifted towards the higher concentrations of methanol. This is connected with the fact that the temperature increase causes a change in the balance between the forces stabilizing and destabilizing the structure of the solution, the latter ones increase with increasing kinetic energy of molecules. One can also note that the absolute values of excess enthalpy at the particular temperatures are higher under higher pressures. This effect is also connected with the balance mentioned above; the pressure increases the forces stabilizing the structure of the solution. A more detailed analysis of the effect of pressure on the excess enthalpy in the system methanol–water will be presented in a subsequent paper.

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