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EXCESS ENTHALPIES OF BINARY POLAR MIXTURES

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ABSTRACT

The measured excess enthalpies of the mixtures of TFE-E181, Water-E181, TFE-Water, Water-Pyridine and Water-Picoline for different temperatures are presented. An isothermal flow-calorimeter was used for the temperatures up to 90°C and a batch calorimeter for the higher temperatures up to 175°C. The superimposed heats of vaporization in the batch calorimeter cell were iteratively determined and used for correction of the measured heats in order to obtain the excess enthalpies. The measured values are then fitted with a modified Redlich-Kister equation. Water-Pyridine and Water-Picoline show a symmetric behavior and are also fitted with an EBLC-model [ref 1,2] for two isotherms. Finally it is discussed how this model can be used to interpolate or extrapolate to other temperatures.

INTRODUCTION

Today different working fluids for ORC – [Organic – Rankine – Cycle] plants and Absorption heat pumps are discussed. In order to fill the lack of information on mixtures, the heats of mixing of TFE (Trifluoroethanol)- E181 (Tetraethylenglycoldimethylenether), H_2O-E181, H_2O-Pyridine, H_2O-Picoline, TFE-H_2O were measured, because they cannot be evaluated from the phase equilibria.

Due to its advantages a flow calorimeter was preferred for the measurements. As the temperature range of the available flow calorimeter was limited to 90°C (water bath thermostat), a batch calorimeter had to be used for higher temperatures up to 175°C. In order to account for the error of the batch calorimeter measurements due to the heats of vaporization a calculating procedure was developed, which corrects the measurements. Both calorimeters are heatflux microcalorimeters making use of the Calvet principle.

Before using the substances they were degassed under vacuum and heated up to the boiling point. In the following text component 1 is always the substance with the lower boiling point and component 2 that with the higher boiling point.

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APPARATUS

Flow calorimeter

For the temperature range from 25^{0}C to 90^{0}C a 4-channel microcalorimeter, called TAM "Thermal Activity Monitor" (LKB, Bromma, Sweden), was used to measure the heats of mixing of binary mixtures. The calorimeter and the cells are described in [ref 3]. One of the four channels is furnished with a "combination measuring cylinder". Fig.1 shows the calorimeter and the flow cell schematically. This cylinder exists of one flow mix (SMZ) and one flow through (RZ) measuring cup, which are connected in series to eliminate every possible disturbing influence. To extend the measuring range the produced voltage from the peltier elements was compensated by a constant voltage, so that measurements up to 0.1 W could be taken. As the vapor pressures of the examined fluids are above 2 bar at the higher temperatures the standard teflon inlet and outlet tubes were changed against stainless steel tubes of the same outer diameter. For the connection of the stainless steel tubes and the gold tubes of the flow cells, the gold tubes were reinforced by

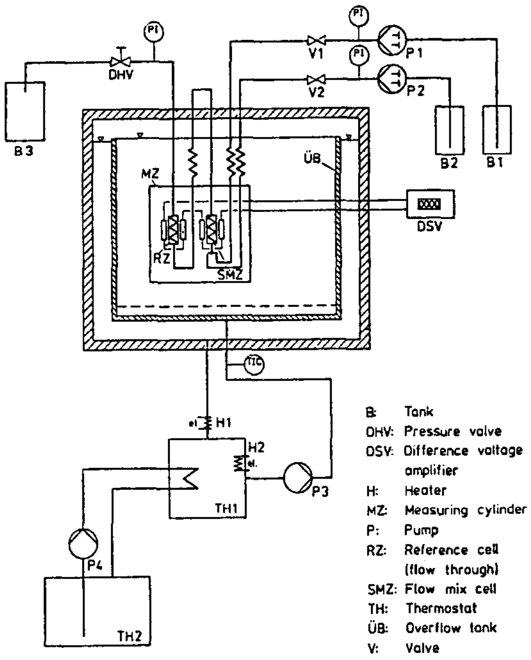


Figure 1: Microcalorimeter TAM with a flow cell in one channel (schematic view)

smaller stainless steel tubes reducing the inner diameter from 1.0 mm to 0.6 mm.

Instead of the proposed Micro Perpex pumps, two HPLC - pumps (LKB, Bromma, Sweden) were installed. These pumps are double piston pumps with nearly no pressure pulsation and cover flow rates from 0.01 ml/min to 5.0 ml/min. Only for the high concentrations the flow rate of 0.01 ml/min or even higher than 0.6 ml/min had to be used. In order to obtain constant pressure in the calorimeter system an overflow valve was fitted at the end of the outlet tube, which expanded the mixed fluid into the tank B3.

The linearity of the measuring signal was tested with a self constructed calibration resistor. A calibration showed that the extended measuring range works linear up to 0.1 W at the same flow rate, however, an influence of the flow rate was indicated above 0.25 ml/min. For that reason a calibration plot was experimentally determined for each liquid and temperature. It proved that the calibration plot could be obtained using the ratio of the specific heats c_p of both liquids. However, there could not be found a temperature relationship.

At the beginning of the experiments the reference system Ethanol/ Water was used for testing the calorimeter and showed good agreement with the results presented in the literature when nearly the same flow rates of both the pumps were adjusted. Great differences in the flow rates, however, produced an influence on the pump with the lower flow rate from the pump with the higher flow rate. For that reason a throttle was inserted downstream of each pump in order to increase the pressure at the pump-pistons, which is now higher than that in the calorimeter system itself, a return flow to the pumps was then stopped. A further advantage was that the HPLC - pumps could operate in a pressure range, above 8 bar, where an automatic compressibility compensation was available. The deviation of the measurements from the literature data were below ± 2%. With this configuration the reported measurements were obtained.

Batch calorimeter

For measurements at temperatures of 150°C and 175°C a batch microcalorimeter BT 2.15 (Setaram, Lyon, France) with a self designed cell was used. Fig.2 shows this cell consisting of a cylindric body with an outer diameter of 17 mm and a length of 80 mm. The cell could be closed with an upper and lower lid. In order to separate the two pure fluids, a lid was located and fixed in the middle of the cell. After temperature equilibrium was obtained, a linkage gear could release a pin thrusting out the separating lid and thus enabling the fluids to mix. By using different cell-bodies, which differ in the position of the seat for the middle lid, different concentrations could be adjusted. By means of turning around the calorimeter over 180° the thrust out middle lid acted as a stirring device. According to the chemical feature of the liquids the O-ring seal material was either Viton or EPDM.

RESULTS

Vapor correction

While the experimental results of the flow calorimeter give the heats of mixing directly, the readings of the batch microcalorimeter are superimposed from the heats of vaporization or condensation at the time of mixing.

Before mixing each chamber of the cell has a vapor and a liquid phase. Therefore, the complete weighed mass of each component consists of the two parts in different states:

$$m_i = m_i^l + m_i^v \qquad (1)$$

Assuming that the gas phases of the two fluids show an ideal mixing behavior, the excess enthalpy of the mixed vapor phase is zero. The heats of mixing of the liquid phase can be calculated from the measurements by:

$$H^E = E \cdot A + \Sigma\, \Delta n_i^v\, |\Delta H_{vi}| + Q_{ST} \qquad (2)$$

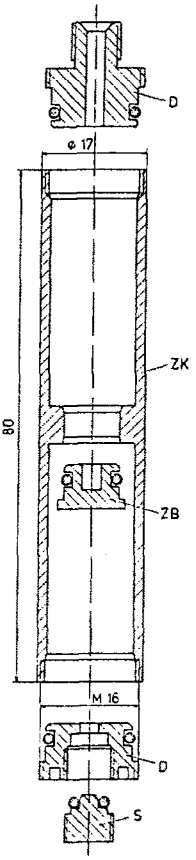


Figure 2: Constructed cell for the batch calorimeter BT 2.15

D: lid; ZB: middle lid for separating the pure fluids; ZK: cell body; S: screw

E stands for the calorimeter-reading and A for the apparatus constant. Q_{St} is the energy of thrusting out the lid, which was determined from experiments with empty cells and cells filled with the same fluid in both the chambers. Δn_i^v is the mole-difference of the vapor phase of the component i before and after the experiment. A positive value means vaporization takes place and a negative value means condensation. The influence of the vaporization enthalpy ΔH_{vi} increases with higher temperatures because the vapor pressures and their differences increase. The vapor phase masses can be calculated by using a cubic EOS, which parameters are fitted to vapor - liquid equilibrium data.

In case the activity coefficients γ could be found in the literature, the real liquid behavior was taken into account, in the other cases ideal behavior was assumed and the activity coefficient set to one.

In Tab.1 the influence of the correction of an Ethanol (1) - Water (2) system is shown.

Table 1: Comparison of the excess enthalpies from Ethanol (1) - Water (2) with data from the literature [ref 5] for t=150°C

x_1	H_m^E (J/mol)			
	uncorrected	ideal corrected	real corrected	literature
0.36480	912.993	885.325	855.752	851.534
0.48470	907.357	981.816	909.173	897.583
0.53748	1044.881	954.675	921.801	883.493
0.76425	668.615	591.149	592.957	608.406

The literature values are taken from Ott [ref 4,5,6], who investigated the heats of mixing of the system Ethanol (1) - Water (2) for different temperatures and pressures with a flow calorimeter. The agreement of the ideal or the real corrected value with the literature data can be recognized. There is a possibility of leakage at the high temperatures, because the temperature of the seals is limited to 200°C, so that a random error may appear. The deviation of the measured value is slightly above 4% if the real correction is applied, in case of the ideal correction it amounts to 8%. These results may provide a feeling for the errors of the following measurements.

Heats of mixing

The measured molar excess enthalpies H_m^E for the different mixtures at different temperatures are summarized in Tab.2. The results were fitted by a modified Redlich-Kister equation (3).

Table 2: Experimental values of H_m^E and their deviation ΔH_m^E from the fit with eq. 3

TFE (1) - E181 (2) T=293.15 K p=0.4 MPa

x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E
-	J/mol	%	-	J/mol	%	-	J/mol	%
.0950	-695.78	-3.66	.1520	-1099.88	-.70	.1520	-1128.31	-3.21
.2030	-1411.25	4.04	.2530	-1870.39	-2.20	.3040	-2090.38	4.48
.3570	-2546.78	-.52	.4330	-3017.70	-.94	.4330	-3028.61	-1.29
.5050	-3301.33	1.62	.5050	-3363.17	-.25	.6040	-3678.48	.61
.6040	-3691.48	.26	.6710	-3780.96	.05	.6710	-3782.10	.02
.6710	-3840.23	-1.49	.6810	-3836.81	-1.45	.6810	-3836.81	-1.45
.6900	-3821.26	-1.18	.6900	-3827.54	-1.34	.7530	-3499.57	3.79
.7530	-3531.18	2.87	.7530	-3592.26	1.12	.8210	-3203.29	.27
.8590	-2816.32	.22	.8590	-2850.64	-.99	.9020	-2203.07	.64
.9480	-1477.03	-9.37						

TFE (1) - E181 (2) T=298.15 K p=0.4 MPa

x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E
-	J/mol	%	-	J/mol	%	-	J/mol	%
.0950	-711.78	-2.96	.1520	-1115.67	-.03	.2030	-1464.68	1.70
.2530	-1812.21	1.87	.3040	-2223.39	-1.24	.3570	-2582.70	-1.62
.4040	-2844.71	-.56	.4660	-3172.50	.11	.5050	-3327.34	1.30
.5500	-3508.92	1.63	.6040	-3722.50	.64	.6470	-3779.91	1.45
.6470	-3854.28	-.51	.6470	-3885.55	-1.31	.6710	-3861.19	-.10
.6810	-3897.62	-.96	.6900	-3903.12	-1.13	.6900	-3906.80	-1.22
.7040	-3900.61	-1.28	.7100	-3805.40	1.02	.7100	-3890.13	-1.18
.7210	-3832.43	-.12	.7310	-3851.01	-1.14	.7530	-3624.98	3.25
.7860	-3589.80	-.00	.8210	-3215.76	3.91	.8590	-2959.08	-.22
.8590	-2976.49	-.80	.9020	-2323.49	.45	.9480	-1518.99	-6.60

TFE (1)- E181 (2) T=323.15 K p=0.4 MPa

x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E
-	J/mol	%	-	J/mol	%	-	J/mol	%
.1020	-763.63	-4.45	.1520	-1141.03	-.78	.2030	-1493.02	1.77
.2530	-1839.88	3.30	.3040	-2280.06	-.30	.3200	-2404.58	-.77
.3570	-2644.12	-.20	.4040	-2937.19	.17	.4550	-3297.48	-1.56
.5050	-3476.10	1.10	.5050	-3513.04	.04	.5050	-3549.15	-.98
.5500	-3656.95	1.84	.5760	-3902.70	-1.90	.6040	-3850.82	1.91
.6040	-3913.15	.29	.6290	-4066.12	-1.81	.6470	-4002.00	.71
.6470	-4118.02	-2.13	.6710	-3939.56	3.14	.7040	-4126.18	-1.35
.7530	-3963.06	.45	.8030	-3702.63	.73	.8300	-3559.07	-1.41
.8590	-3162.56	.94	.9020	-2519.35	.93	.9480	-1616.10	-3.55

Table 2: continued

TFE (1) - E181 (2) T=348.15 K p=0.4 MPa

x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m
-	J/mol	%	-	J/mol	%	-	J/mol	%
.1020	-799.00	-2.51	.2030	-1554.33	2.43	.3040	-2414.52	-1.72
.4040	-3070.98	.47	.5050	-3638.77	2.12	.5500	-4008.21	-1.36
.5500	-4014.99	-1.53	.6040	-4138.15	1.14	.6040	-4138.15	1.14
.6560	-4377.00	-1.06	.7040	-4436.00	-1.47	.7530	-4286.43	-.03
.8030	-3956.60	1.64	.8030	-3979.67	1.05	.9240	-2346.64	-2.79

TFE (1) - E181 (2) T=363.15 K p=0.4 MPa

x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m
-	J/mol	%	-	J/mol	%	-	J/mol	%
.0950	-780.17	-4.29	.1520	-1230.42	-.05	.2030	-1601.89	3.81
.2530	-2113.54	-1.61	.3040	-2489.90	.03	.3570	-2897.66	.03
.4040	-3163.95	-2.43	.4490	-3598.01	-1.39	.4550	-3637.58	-1.38
.5050	-3923.10	-.70	.5500	-4180.69	-1.01	.6040	-4307.16	1.49
.6470	-4420.64	1.69	.6960	-4456.04	2.03	.7040	-4610.73	-1.45
.7100	-4520.35	.43	.7240	-4533.26	-.26	.7530	-4441.48	.06
.7770	-4397.30	-1.43	.7770	-4411.57	-1.75	.8030	-4117.41	1.06
.8590	-3629.14	-2.00	.9020	-2766.53	2.23	.9020	-2788.60	1.42
.9520	-1612.90	.25						

TFE (1) - E 181 (2) T=448.15 K p=ps

x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m
-	J/mol	%	-	J/mol	%	-	J/mol	%
.0955	-1038.10	8.95	.1903	-2164.85	1.00	.3524	-3545.69	8.50
.3844	-4658.88	-11.11	.4653	-4791.94	0.20	.4977	-4933.23	1.80
.5430	-5388.52	-2.10	.5925	-5262.79	3.80	.6981	-5487.40	-0.72
.7946	-4564.29	4.28	.9061	-3149.48	-9.73			

H_2O (1) - E181 (2) T=298.15 K p=0.4 MPa

x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m
-	J/mol	%	-	J/mol	%	-	J/mol	%
.0750	81.91	-9.11	.0890	86.82	-6.11	.1090	89.35	-.65
.1270	81.91	-.63	.1500	64.73	-2.16	.2020	8.91	23.74
.2530	-84.23	-12.33	.2990	-146.62	8.91	.3030	-162.08	3.40
.3510	-269.50	-.82	.4040	-372.80	3.63	.4480	-489.19	.64
.5040	-636.37	.37	.5490	-777.83	-1.19	.6040	-970.06	-2.45
.6520	-1138.45	-1.47	.7090	-1351.42	.27	.7530	-1525.45	1.52
.8020	-1728.58	1.81	.8590	-1946.27	-.35	.9010	-1965.06	-1.61
.9240	-1826.22	-.14	.9480	-1577.98	-.60	.9730	-1021.03	3.24

Table 2: continued

H_2O (1) - E181(2) T=323.15 K p=0.4 MPa

x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m
-	J/mol	%	-	J/mol	%	-	J/mol	%
.0750	137.53	-17.56	.1090	187.85	-8.58	.1500	230.86	-1.24
.2020	257.69	5.77	.2530	258.41	12.85	.2990	189.75	.06
.3010	177.54	-5.72	.3510	129.10	.13	.4040	46.05	1.27
.4480	-44.90	-9.53	.5040	-178.85	-3.00	.5490	-308.86	-2.70
.6040	-488.08	-1.26	.6520	-668.78	-.70	.7090	-903.03	.34
.7530	-1090.06	1.36	.8020	-1299.52	1.62	.8590	-1522.37	-.77
.9010	-1553.72	-1.47	.9240	-1447.00	.40	.9480	-1263.41	-.66
.9730	-823.54	2.71						

H_2O (1) - E181 (2) T=348.15 K p=0.4 MPa

x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m
-	J/mol	%	-	J/mol	%	-	J/mol	%
.0750	202.69	-4.68	.1090	283.20	-2.32	.1500	368.18	.08
.2020	444.94	.55	.2530	488.69	.04	.2990	518.42	2.32
.3510	504.48	1.14	.4040	459.08	-.09	.4480	400.06	-.48
.5040	285.42	-3.46	.5490	175.35	-3.82	.6040	8.72	-25.17
.6520	-167.24	-.74	.7090	-398.39	1.33	.7530	-590.02	1.61
.8020	-803.31	1.35	.8590	-1028.37	-1.21	.9010	-1097.22	-2.30
.9240	-1003.59	3.08	.9480	-920.85	-1.45	.9730	-613.05	1.23

H_2O (1) - E181 (2) T=363.15 K p=0.4 MPa

x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m
-	J/mol	%	-	J/mol	%	-	J/mol	%
.1090	343.32	-1.69	.1500	445.19	-1.25	.2010	559.50	1.11
.2530	619.38	-1.64	.2990	685.53	1.95	.3510	696.39	.79
.4040	682.19	.81	.4480	632.80	-.87	.5040	553.38	-.05
.5490	444.53	-2.64	.6040	305.47	1.13	.6520	124.37	-10.49
.7090	-78.31	14.03	.7530	-280.03	.13	.8020	-481.80	2.90
.8590	-713.10	-.07	.9010	-814.75	-2.00	.9480	-708.04	-.19
.9730	-480.33	2.36						

H_2O (1) - E 181 (2) T=423.15 K p=ps

x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m
-	J/mol	%	-	J/mol	%	-	J/mol	%
.1013	516.81	19.44	.2109	904.77	-0.08	.2765	1038.79	-11.84
.3963	1503.51	1.65	.4405	1551.73	1.19	.4945	1624.87	4.62
.5464	1445.65	-4.69	.6114	1401.71	0.22	.6609	1264.91	0.01
.6904	1208.56	3.29	.7454	932.96	-3.31	.8166	754.21	11.53
.8314	520.615	-15.93	.8892	345.206	-4.93			

Table 2: continued

H_2O (1) - E 181(2) T=448.15 K p=ps

x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m
-	J/mol	%	-	J/mol	%	-	J/mol	%
.1087	372.79	-30.0	.2076	1090.84	6.92	.3080	1564.13	2.75
.3501	1725.55	1.41	.4086	1858.01	-2.51	.5219	2114.06	0.23
.5575	2059.01	-2.73	.6097	2066.75	-0.18	.7068	1832.29	0.75
.8140	1382.61	5.63	.9050	641.19	-11.04			

H_2O (1) - Picoline (2) T=298.15 K p=0.4 MPa

x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m
-	J/mol	%	-	J/mol	%	-	J/mol	%
.0750	-329.53	-6.90	.1740	-844.87	1.04	.2740	-1428.89	.53
.3780	-1941.18	.57	.4770	-2278.30	-.23	.5490	-2383.21	-.55
.5780	-2388.01	-.62	.5990	-2359.40	.11	.5990	-2360.79	.05
.6210	-2337.40	.02	.6860	-2190.49	.08	.6860	-2197.60	-.24
.7320	-2015.11	.34	.7850	-1741.75	.89	.8450	-1348.74	1.75
.8910	-1024.95	-.58	.9560	-467.15	-5.79	.9560	-468.01	-5.96

H_2O (1) - Picoline (2) T=323.15 K p=0.4 MPa

x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m
-	J/mol	%	-	J/mol	%	-	J/mol	%
.0750	-235.62	-.56	.1000	-330.11	.23	.1390	-485.23	1.81
.1390	-500.29	-1.26	.1800	-679.71	-.51	.2150	-838.98	-.39
.2610	-1042.73	.09	.3320	-1339.35	.28	.4060	-1597.45	.24
.4770	-1769.20	.22	.5490	-1854.24	-.12	.5490	-1854.24	-.12
.5780	-1857.53	-.21	.5990	-1870.01	-1.42	.6100	-1823.20	.61
.6100	-1827.54	.37	.6860	-1688.14	.57	.7320	-1551.46	.13
.7850	-1346.86	-1.06	.8450	-999.58	1.97	.8450	-1012.95	.62
.9160	-591.12	-2.10	.9560	-318.30	-3.39			

H_2O (1) - Picoline (2) T=348.15 K p=0.4 MPa

x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m
-	J/mol	%	-	J/mol	%	-	J/mol	%
.0750	-128.12	-1.75	.1000	-188.55	-1.71	.1390	-289.83	.41
.1800	-405.60	2.21	.2150	-531.22	-.96	.2610	-678.78	-.52
.3320	-894.71	.10	.4060	-1084.46	.39	.4770	-1215.39	.13
.5490	-1276.14	-.25	.5780	-1270.19	.12	.6100	-1256.32	-.20
.6860	-1149.03	-.66	.7320	-1040.10	-1.18	.7850	-827.63	3.84
.8450	-616.58	2.37	.8450	-643.90	-1.97	.8910	-454.08	-3.14
.9360	-259.76	-3.78	.9650	-113.52	-6.15	.9650	-141.26	-6.66

Table 2: continued

H_2O (1) - Picoline (2) T=363.15 K p=0.4 MPa

x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E
-	J/mol	%	-	J/mol	%	-	J/mol	%
.0750	-60.55	9.13	.1000	-98.28	3.94	.1390	-170.35	-.24
.1800	-255.57	-.86	.2150	-335.07	-1.03	.2610	-444.57	-1.04
.3320	-607.54	-.16	.4060	-756.24	.39	.4770	-861.22	.46
.5490	-909.65	.67	.5780	-911.29	.65	.6100	-900.78	.51
.6460	-877.30	-.26	.6460	-897.90	-2.55	.6860	-818.23	.27
.7320	-732.73	-.09	.7850	-607.28	-1.01	.8450	-407.07	4.74
.8450	-411.92	3.51	.8450	-433.94	-1.74	.8910	-293.94	-3.11
.9320	-173.86	-6.10	.9650	-70.58	7.16			

H_2O (1) - Picoline (2) T=423.15 K p=ps

x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E
-	J/mol	%	-	J/mol	%	-	J/mol	%
.0757	364.11	10.03	.0860	312.01	-14.75	.1609	566.93	2.45
.2689	609.77	-4.91	.3889	664.78	4.48	.3976	637.44	-2.50
.5022	771.36	-0.43	.5189	815.85	6.85	.6637	627.79	-8.36
.8087	462.561	-6.99	.9194	420.882	21.54			

H_2O (1) - Picoline (2) T=448.15 K p=ps

x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E
-	J/mol	%	-	J/mol	%	-	J/mol	%
.0948	534.38	-2.53	.1865	763.67	-3.23	.2647	1053.80	1.18
.4154	1371.48	-4.60	.4916	1546.88	3.80	.5599	1477.71	1.70
.6288	1365.76	-1.72	.6846	1257.93	-3.35	.7841	987.05	-4.68
.9289	684.418	19.90						

H_2O (1) - Pyridine (2) T=298.15 K p=0.4 MPa

x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E
-	J/mol	%	-	J/mol	%	-	J/mol	%
.1000	-263.67	-7.41	.1820	-578.34	-1.31	.2550	-882.16	1.24
.3080	-1102.71	1.53	.3580	-1296.76	1.27	.4070	-1468.88	.36
.4470	-1586.23	-.45	.4970	-1687.70	-.98	.5600	-1743.35	-1.42
.5970	-1723.47	-.88	.6400	-1671.94	-.70	.6900	-1519.75	2.35
.7480	-1353.04	1.33	.8170	-1055.95	1.52	.8560	-881.94	-1.33
.8990	-603.12	3.81	.9470	-359.90	-7.14	.9470	-379.21	-11.87

Table 2: continued

H_2O (1) - Pyridine (2) T=323.15 K p=0.4 MPa

x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E
-	J/mol	%	-	J/mol	%	-	J/mol	%
.1000	-174.49	-2.60	.1510	-322.72	-1.80	.2030	-490.65	-.29
.2480	-643.39	.41	.3080	-844.20	.82	.3580	-997.74	.92
.4070	-1131.96	.45	.4470	-1221.67	.01	.4970	-1304.44	-.71
.5600	-1342.15	-.92	.5970	-1332.12	-1.06	.6400	-1268.82	.39
.6900	-1179.95	.15	.7480	-1010.74	1.33	.8170	-751.50	3.41
.8560	-625.87	-1.50	.8990	-440.45	-2.51	.9470	-237.54	-7.99

H_2O (1) - Pyridine (2) T=348.15 K p=0.4 MPa

x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E
-	J/mol	%	-	J/mol	%	-	J/mol	%
.1000	-70.80	-2.94	.1510	-161.31	-1.71	.2030	-273.57	-.08
.2480	-381.50	.39	.3080	-528.59	.57	.3580	642.73	.75
.4070	-745.65	.08	.4470	-812.67	-.16	.4970	-872.55	46
.5600	-899.98	-.40	.5970	-891.39	-.38	.6400	-854.78	-.03
.6900	-785.38	-.07	.7480	-658.10	1.26	.8170	-475.49	2.07
.8560	-376.89	-1.34	.8990	-252.43	-2.70	.9470	-118.36	-3.20

H_2O (1) - Pyridine (2) T=363.15 K p=0.4 MPa

x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E
-	J/mol	%	-	J/mol	%	-	J/mol	%
.1000	-9.13	-24.72	.1510	-56.24	3.21	.2030	-133.11	.38
.2480	-212.06	-.21	.3080	-323.85	-.13	.3580	-413.62	.25
.4070	-494.73	-.00	.4470	-549.19	-.05	.4970	-597.49	.03
.5600	-623.68	-.14	.5970	-617.92	-.21	.6400	-588.75	.10
.6900	-532.13	-.12	.7480	-429.82	.91	.8170	-290.92	-.76
.8560	-201.09	.73	.8990	-117.11	-2.64	.9470	-35.02	4.77

H_2O (1) - Pyridine (2) T=423.15 K p=ps

x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E
-	J/mol	%	-	J/mol	%	-	J/mol	%
.0732	188.79	-5.72	.1858	420.69	6.65	.2748	476.89	-0.96
.2907	475.66	-3.71	.3704	519.76	-3.78	.4978	609.92	4.49
.5120	594.99	1.63	.5835	588.52	-0.62	.6570	584.88	0.23
.7062	565.76	0.12	.8139	427.92	-9.93	.9324	284.41	18.67

H_2O (1) - Pyridine (2) T=448.15 K p=ps

x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E
-	J/mol	%	-	J/mol	%	-	J/mol	%
.1121	448.66	2.65	.1620	588.78	1.30	.2827	796.24	-5.62
.4221	1058.08	2.76	.4709	1084.56	1.21	.5215	1103.69	0.15
.6049	1125.744	0.70	.7256	979.64	-5.84	.7918	958.562	4.11
.8053	867.28	-2.27	.9207	499.87	5.85			

Table 2: continued

TFE (1) - H_2O (2) T=298.15 K p=0.4 MPa

x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m
-	J/mol	%	-	J/mol	%	-	J/mol	%
.0145	-74.62	15.73	.0245	-113.03	5.89	.0401	-146.83	-2.69
.0478	-142.31	1.55	.0478	-148.90	-2.94	.0772	-109.61	3.74
.1115	-23.26	65.77	.2006	175.63	-11.28	.2006	197.73	1.16
.2507	322.41	1.30	.2949	423.85	1.61	.3342	497.81	.18
.4676	695.42	-.69	.5009	728.81	-.25	.5565	764.66	.61
.6009	764.48	.13	.6372	751.54	-.23	.7901	593.98	.00

TFE (1) - H_2O (2) T=323.15 K p=0.4 MPa

x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m
-	J/mol	%	-	J/mol	%	-	J/mol	%
.0099	-20.91	20.53	.00994	-1.21	18.82	.01455	-27.49	11.89
.01761	-30.62	6.71	.02448	-33.69	-3.30	.04779	-.37	-24.19
.04779	-14.91	-98.12	.07719	85.07	10.17	.11149	179.69	.28
.20061	418.94	1.08	.25071	514.07	-.89	.29491	588.12	-1.81
.36931	732.93	2.51	.42950	781.68	-1.03	.55649	865.78	-.16
.60091	860.68	.07	.66751	812.12	-.02	.79011	618.73	.35
.82663	534.38	-.21	.88275	392.49	-.14			

TFE (1) - H_2O (2) T=348.15 K p=0.4 MPa

x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m
-	J/mol	%	-	J/mol	%	-	J/mol	%
.04779	107.79	-8.94	.07719	217.30	2.50	.11149	331.78	1.77
.20061	578.65	-.78	.25071	686.06	-.43	.33418	813.97	.56
.38552	857.78	.11	.50095	883.81	-2.24	.50095	920.08	1.79
.60091	869.15	.22	.66751	793.95	-.05	.88275	350.52	-.01

TFE (1) - H_2O (2) T=348.15 K p=6 MPa

x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m	x_1	H^E_m(exp)	ΔH^E_m
-	J/mol	%	-	J/mol	%	-	J/mol	%
.04779	107.81	-6.10	.04779	108.72	-5.21	.04779	111.80	-2.32
.07719	213.61	2.00	.07719	214.73	2.51	.11149	331.19	2.07
.20061	576.37	-1.03	.25071	684.99	-.43	.33418	812.25	.25
.33418	813.62	.41	.38552	859.75	-.10	.50095	914.25	.05
.60091	870.84	-.38	.66751	796.11	.30	.88275	347.99	-.50
.88275	351.18	.42						

Table 2: continued

TFE(1) - H_2O (2) T=363.15 K p=0.4 MPa

x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E
-	J/mol	%	-	J/mol	%	-	J/mol	%
.02448	59.98	-29.29	.02448	66.00	-17.50	.02448	68.06	-13.94
.04779	167.36	5.26	.05903	185.10	-7.39	.05903	198.67	-.05
.07719	285.09	7.39	.11149	408.93	6.03	.20061	616.58	-5.05
.20061	625.70	-3.52	.20061	635.86	-1.86	.20061	643.66	-.63
.20061	647.81	.02	.20061	649.32	.25	.20061	653.63	.91
.20061	653.71	.92	.20061	657.46	1.48	.25071	769.12	1.68
.29491	839.22	1.24	.36931	931.87	2.57	.42950	902.06	-3.88
.42950	921.26	-1.72	.42950	956.29	2.01	.46761	925.07	-1.66
.46761	957.67	1.80	.50095	901.24	-3.64	.50095	906.54	-3.03
.50095	926.25	-.84	.50095	940.54	.69	.50095	951.50	1.84
.50095	955.36	2.23	.50095	956.47	2.35	.55649	900.14	-.40
.55649	918.39	1.60	.60091	858.45	-.41	.66751	774.82	.32
.71506	686.18	-.74	.75071	625.80	.37			

TFE (1) - H_2O (2) T=398.15 K p=ps

x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E
-	J/mol	%	-	J/mol	%	-	J/mol	%
.0928	463.11	2.72	.11017	503.917	2.53	.1979	773.371	0.02
.1996	770.00	-0.95	.3065	910.60	-2.60	.3139	934.31	-0.58
.3480	975.40	1.90	.4221	984.56	3.23	.4971	910.09	1.17
.5910	763.62	-2.04	.5986	779.57	1.56	.6308	698.83	-2.27
.6934	563.09	-6.89	.7293	549.69	3.19	.7964	377.16	-5.30
.8004	390.69	0.47	.8666	319.41	20.46	.8906	181.71	-13.31

TFE (1) - H_2O (2) T=423.15 K p=ps

x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E
-	J/mol	%	-	J/mol	%	-	J/mol	%
.0484	336.44	3.40	.1064	653.62	5.84	.2520	969.82	-0.40
.3157	960.81	-4.86	.3589	993.30	-0.72	.3806	994.71	0.54
.4189	967.21	0.78	.4637	901.71	-1.06	.4650	928.53	2.02
.5631	769.03	0.06	.6115	691.28	0.39	.6258	667.63	0.48
.6269	653.56	-1.37	.6834	609.13	7.29	.8268	252.66	-24.62
.8565	286.18	8.07						

TFE (1) - H_2O (2) T=448.15 K p=ps

x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E	x_1	H_m^E(exp)	ΔH_m^E
-	J/mol	%	-	J/mol	%	-	J/mol	%
.0909	629.70	11.11	.1949	871.94	-6.05	.3039	1069.96	-0.23
.3419	1072.45	-0.86	.3472	1113.61	2.89	.4179	1004.17	-4.64
.5432	911.77	1.34	.5756	844.46	-0.34	.5903	871.47	5.64
.6231	796.637	4.07	.6800	621.77	-5.82	.7990	371.99	-13.63
.9067	241.081	16.31						

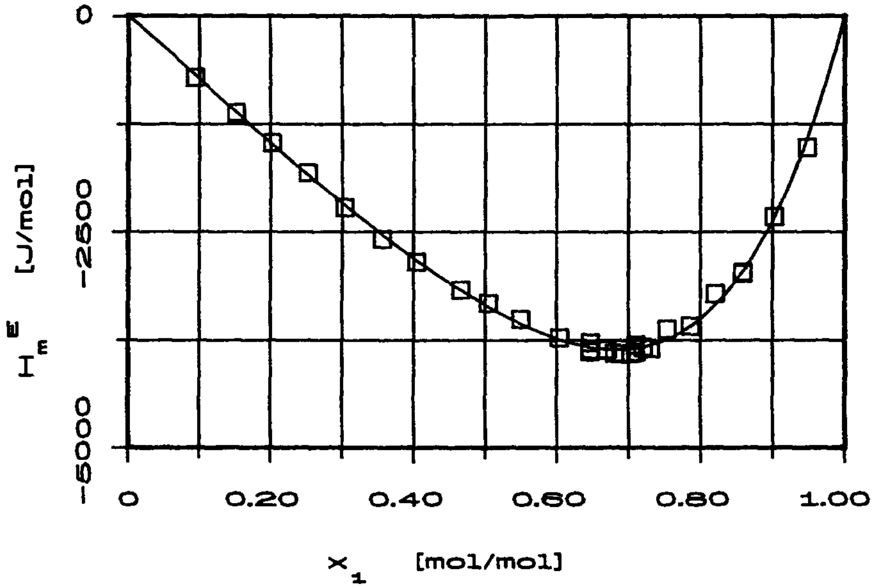


Figure 3: Excess enthalpies of TFE (1) - E181 (2) for t= 25°C [□]

$$H_m^E = x_1 (1 - x_1) \sum_{i=0}^{n} A_i (2x_1 - 1)^i / [1-k(1-2x_1)] \tag{3}$$

A_i are the fitted coefficients and shown in table 3. For the asymmetric curves with points of inflection the value of k is unequal zero, and the number of coefficients is 6. In the other cases 4 coefficients are used and k is zero.

Fig.3 shows the results of TFE (1) - E181 (2) at 25°C. The points are the measured values. The minimum at x_1 = 0.7 was measured with different flow rates to check the reproducibility. The dependence of the temperature is interesting, since with increasing temperature the excess enthalpies decrease, see Fig.4, which gives fitted curves to measured values. The deviation of the measured values from the fit is presented in Fig.5. While the fit of the 25°C, 50°C, 75°C and 90°C isotherms deviates up to ± 2%, it increases up to ± 4% for the 150°C and 175°C. The reason can be that the activity coefficient of E181 was determined applying the UNIFAC - method.

The results of H_2O (1) - E181 (2) are presented in Fig.6. These curves are typical for a mixture with water. At lower temperatures the minimum

Table 3: Coefficients of a modified Redlich-Kister fit (eq.3) with standard deviation σ

t	25°C	50°C	75°C	90°C	150°C	175°C
TFE-E181						
A (0)	-13387.89	-13956.02	-14750.30	-15465.84	20038.96	-20145.89
A (1)	-9203.31	-10188.61	-11422.95	-11749.31	-11688.61	-12528.6
A (2)	-4840.40	-6774.21	-7736.30	-7575.87	-9228.10	-4710.58
A (3)	-2356.85	-4306.11	-4075.80	-4204.18	0.0	0.0
K	0.0	0.0	0.0	0.0	0.0	0.0
σ [J/mol]	55	50	50	50	253.26	226.03
H_2O-E181						
A (0)	-2511.10	-652.36	1216.70	2244.22	6193.55	8364.92
A (1)	-3447.41	-4638.20	-5381.91	-5466.85	-630.71	2136.79
A (2)	-788.23	-963.67	-1269.84	-1277.03	-3342.63	-2760.39
A (3)	-3772.86	-2161.83	-490.61	-296.86	0.0	0.0
K	-0.80	-.80	-0.81	0.0	0.0	0.0
σ [J/mol]	15	14	11	9	61.9	58.21
TFE-H_2O						
A (0)	2919.71	3396.02	3641.24	3737.32	3455.01	3849.56
A (1)	3826.25	3803.57	310.86	-635.98	-2789.70	-2684.87
A (2)	-159.15	113.70	923.15	-230.32	1327.95	1086.52
A (3)	-666.50	-1865.96	-538.92	-705.97	26.02	39.24
A (4)	828.50	-132.98	-3327.15	-8.13	0.0	0.0
A (5)	2188.48	2218.11	-567.91	1911.42	0.0	0.0
K	0.78	0.78	0.0	0.0	0.0	0.0
σ (J/mol)	7	7	11	16	26.0	39.2
H_2O-Pyridine						
A (0)	-6700.86	-5193.35	-3484.14	-2399.30	2332.01	4363.10
A (1)	-2636.31	-2058.10	-1620.82	-1409.88	406.85	1171.98
A (2)	2967.31	2950.41	2740.27	2715.96	1315.77	1551.27
A (3)	39.42	448.69	644.23	1060.92	0.0	0.0
K	0.0	0.0	0.0	0.0	0.0	0.0
σ [J/mol]	20	11	4	2	24.36	29.16
H_2O-Picoline						
A (0)	-9270.00	-7237.55	-4974.50	-3552.92	2709.87	5139.87
A (1)	-3330.36	-2722.38	-1969.72	-1733.32	-338.43	634.16
A (2)	2514.68	2505.35	2677.05	2430.35	1672.95	1286.82
A (3)	325.80	429.81	730.05	1023.88	0.0	0.0
K	0.0	0.0	0.0	0.0	0.0	0.0
σ [J/mol]	4	9	10	8	38.6	47.8

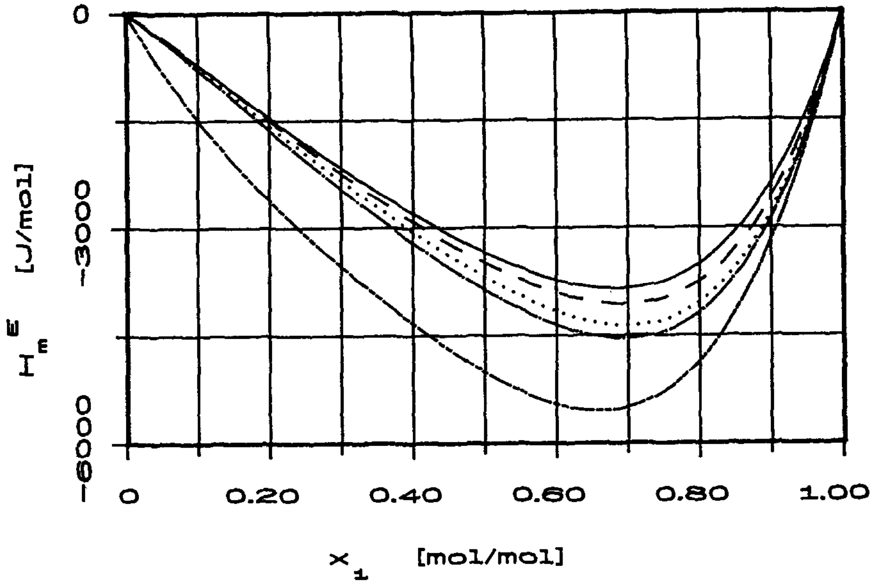
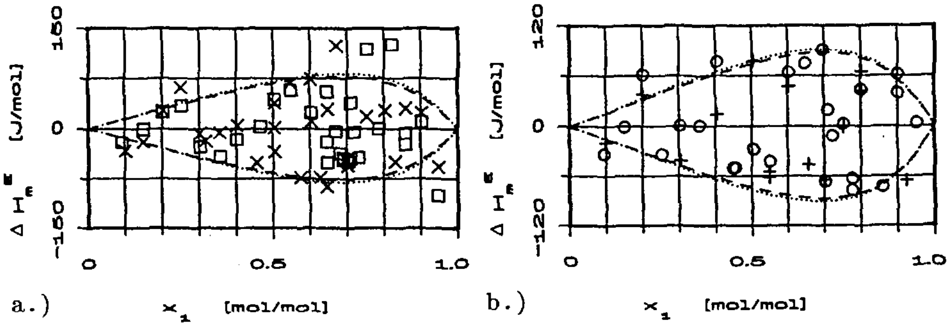
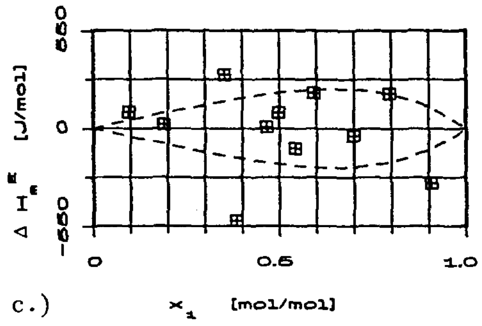


Figure 4: Equation 3 fitted to measured excess enthalpies of TFE (1) - E181 (2) for temperatures 25°C (——); 50°C (– – –), 75°C (· · · ·), 90°C (–·–·–), 175°C (–··–·)



a.)

b.)



c.)

Figure 5: Deviation of experimental results from eq. 3 for TFE (1) - E181 (2)

a : (□) t= 25°C and (×) t= 50°C;

b : (+) t= 75°C and (o) t= 90°C

c : (⊞) t= 175°C

a,b : dashed lines give the 2% error of the lower and dotted lines of the higher temperature

c: dashed lines give the 4% error of t=175°C

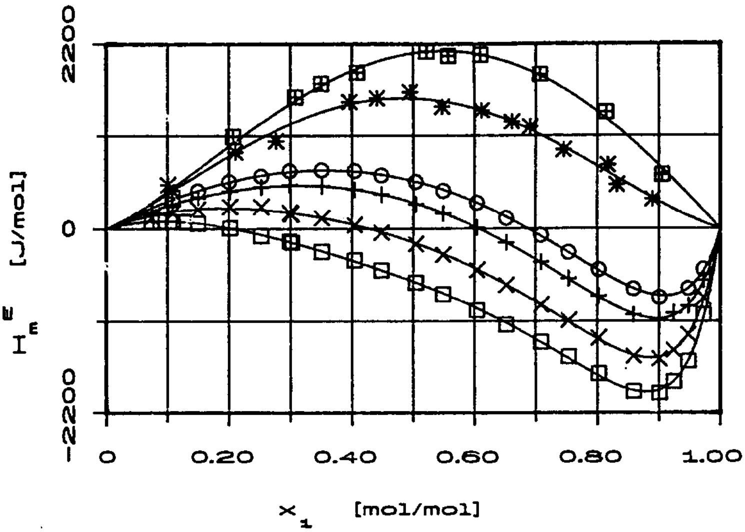
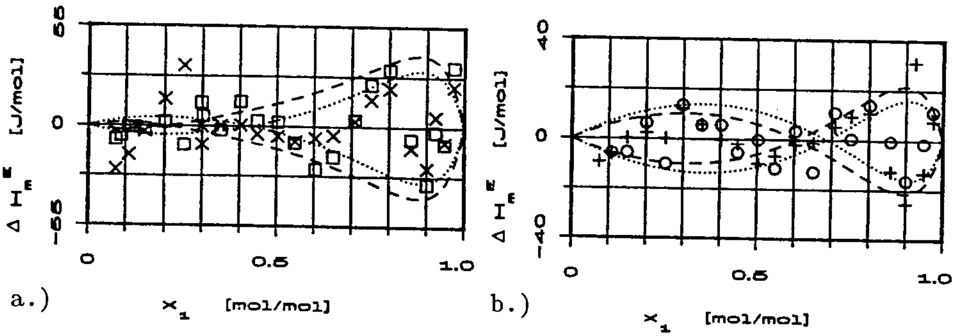


Figure 6: Measured excess enthalpies of H_2O (1) – E181 (2) fitted to eq.3 for temperatures 25°C (□); 50°C (×); 75°C (+); 90°C (o); 150°C (✱), 175°C (⊞)



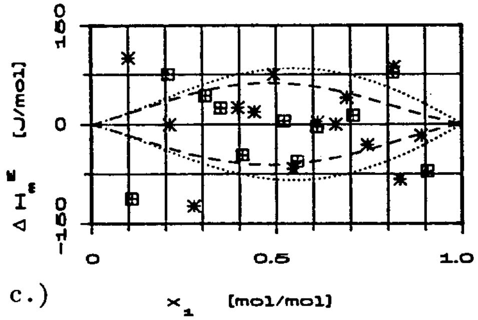


Figure 7: Deviation of experimental results from eq.3 for H_2O (1) – E181 (2)

a : (□) t= 25°C and (×) t= 50°C;

b : (+) t= 75 C and (o) t= 90°C

c : (✱) t= 150°C and (⊞) t= 175°C

a,b : dashed lines give the 2% error of the lower and dotted lines of the higher temperature

c : dashed lines give the 4% error of the lower and the dotted lines of the higher temperature is displaced on the water rich side near to x_1 = 0.9, (the same for alc hol - water - mixtures). With increasing temperature the excess entha py curves are shifting more and more to positive values and have thei maximum at x_1 = 0.5 like a regular mixture. The deviations are shown i Fig.7.

The molar excess enthalpies of the TFE (1) - Water (2) system, a fi of eq.3 is plotted in Fig.8, show a similar shape but with a lower te perature dependence. The minimum is reflected to the other side b cause in this case the water is the less volatile component 2. The min mum of the water rich side indicates the destruction of the water stru ture at a defined addition of the other component mentioned by Larki [ref 7] for the Ethanol - Water system. The concentration for the d struction is dependent on shape, size and interaction energies of th alcohol component. The intersection point of the curves must b pointed out. Cooney and Marcon [ref 8] have measured this system for temperatures from 25°C up to 65°C with also such intersection points. A there is only a low dependence of H_m^E from temperatures between 90°C and 125°C but a great shift of the maximum to the left side, the lowe temperatures were measured with the flow and the batch calorimeter t eliminate a systematical error.

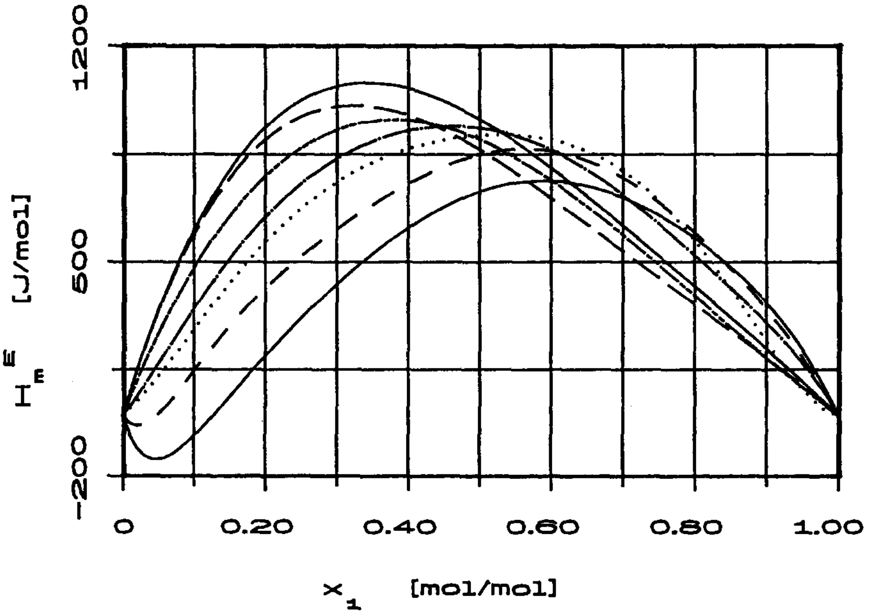
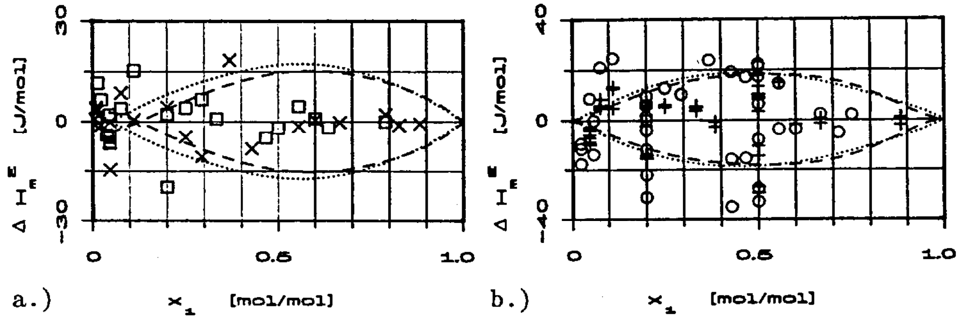


Figure 8:Fit of eq.3 to measured excess enthalpies of TFE (1) - H_2O (2 for temperatures 25°C (——); 50°C (---); 75°C (····); 90° (-·-·-); 125°C (-··-··); 150°C (--) and 175°C (———)



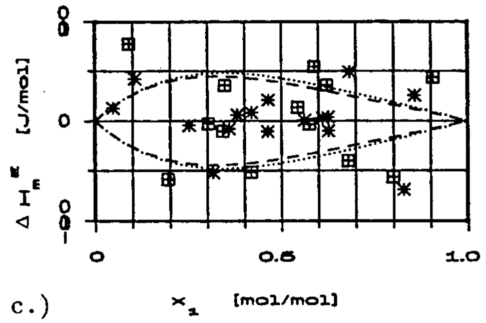


Figure 9: Deviation of experimental results from eq.3 for TFE (1) - H_2O (2)

a : (□) t= 25°C and (×) t= 50°C;

b : (+) t= 75°C and (o) t= 90°C

c : (∗) t= 150°C and (⊞) t= 175°C

a,b : dashed lines give the 2% error of the lower and dotted lines of the higher temperature

c: dashed lines give the 4% error of the lower and the dotted lines of the higher temperature

But all measured isotherms of both calorimeters overlap in their error bounds. The deviation of the measured values from the fit are presented in Fig.9. A pressure dependence between 0.4 MPa and 6 MPa was not observed.

Discussion

Purely for better representation of the measured data, the results of the three binary systems were fitted to a Redlich - Kister equation (eq.3). Now an Enthalpy - Based - Local - Composition - model (EBLC - model) will be discussed. It was developed by Rowley and Battler [ref 1,2] who used the following equation

$$H_m^E = x_1\ x_2 \left[\sum_{i=1}^{2} \sum_{j=1}^{2} \left[h_{ji}\ G_{ji} \Big/ \left[\sum_{k=1}^{2} x_k\ G_{ki} \right] \right] + b\ (T-\ 300) \right]_{i \neq j} \qquad (4)$$

$$G_{ji} = \exp\ (-\ a_{ji}/RT); \qquad G_{11} = 1; \qquad G_{22} = 1; \qquad (5)$$

whose form is analogous to the NRTL equation for G_m^E. This equation consists of 5 temperature independent coefficients. The value 300 K in the

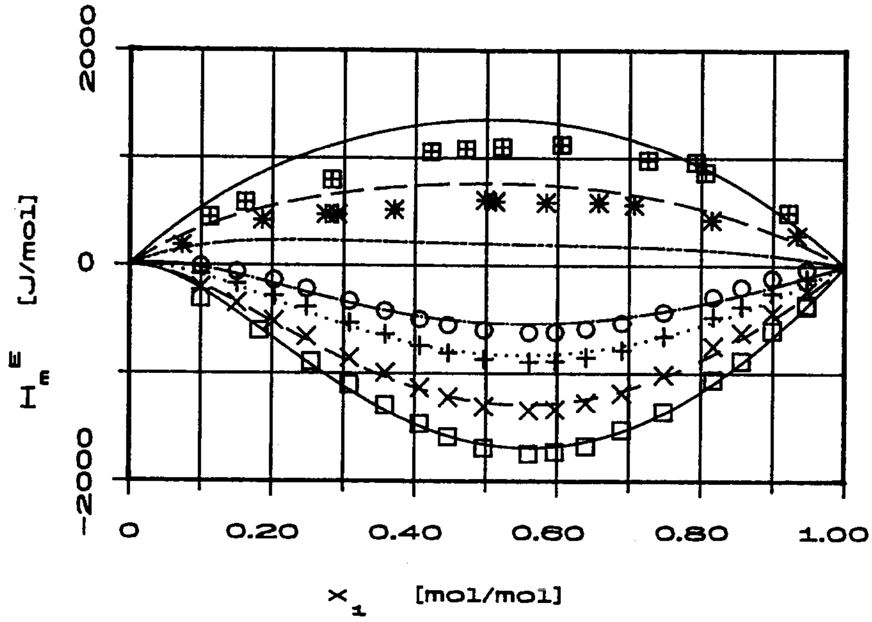


Figure 10: Measured excess enthalpies of H_2O (1) - Pyridine (2) for t= 25°C (□) ; 50°C (×) ; 75°C (+) ; 90°C (o) ; 150°C (∗) , 175°C (⊞) The isotherms of t=25°C and 50°C are fitted to eq.4, the others are calculated from the determined parameters

temperature dependent term corresponds to the reference temperature and can be varied. Most of the H_m^E-values are given for 25°C and one other temperature. Therefore the reference temperature of 300 K was used.

For the Water (1) - Pyridine (2) system only the measured excess enthalpies for t= 25°C and t= 50°C were used to evaluate the coefficients of eq.4, which are given in Tab.6. All isotherms in Fig.10 are then

Table 6: Coefficients for the EBLC - model
The isotherms of t= 25°C and t= 50°C were fitted.

system		Water - Pyridine	Water - Picoline
h_{12}	(J/mol)	-52647.37	-92158.70
h_{21}	(J/mol)	21989.71	48272.68
a_{12}	(J/mol)	1468.46	1122.17
a_{21}	(J/mol)	-2184.47	-1536.73
b	(J/mol K)	132.10	181.54

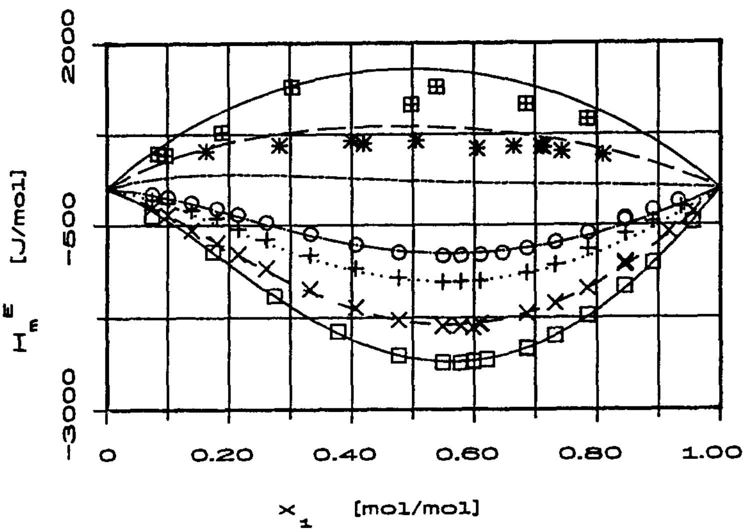


Figure 11: Measured excess enthalpies of H_2O (1) - Picoline (2) for t= 25°C (□); 50°C (x); 75°C (+); 90°C (o); 150°C (*), 175°C (⊞) The isotherms of t=25°C and 50°C are fitted to eq. 4, the other are calculated from the determined parameters

calculated from eq.4. The isotherms of t=75°C and 90°C are in a good agreement with the measured points, whereas with increasing temperature the deviation increases reaching nearly 20% at t=175°C for the maximum.

In the same way the EBLC-model was used for the Water (1) - Picoline (2) system in Fig.11. The deviation at the minimum of the 25°C isotherm is below -1% while the deviation of the 50°C isotherm is -2%. For the extrapolated isotherms of 75°C and 90°C the error of calculated H^E_m increase up to 10% and for the isotherms of 150°C and 175°C up to 20%. On both sides of the curves the percentage deviation is higher. For the Water (1) - Picoline (2) system the deviation of the minimum at t= 90°C is only -3%.

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