ELSEVIER

Thermochimica Acta 310 (1998) 87–94

thermochimica acta

Effect of NaCl on the excess enthalpies of binary liquid systems[1]

T. Friese, S. Schulz, P. Ulbig*, K. Wagner

Universität Dortmund, Lehrstuhl für Thermodynamik, D-44221 Dortmund, Germany

Received 29 April 1997; accepted 16 June 1997

Abstract

The excess molar enthalpies h^E_{1+23} of ethanol+(water+NaCl), benzylalcohol+(water+NaCl), and cyclohexane+(methanol+NaCl) were measured at 298.15 K, those of methanol+(water+NaCl) at 298.15 and 323.15 K. An LKB flow microcalorimeter was used and a special flow-mix cell was developed with regard to the corrosive electrolyte solutions. Knowing the integral enthalpy of solution and the solution enthalpy at infinite dilution for a salt (3) in a solvent (2), the molar excess enthalpy h^E_{123} can be calculated. © 1998 Elsevier Science B.V.

Keywords: Alcohol; Cyclohexane; Excess enthalpies; Flow calorimetry; Sodium chloride; Water

---

1. Introduction

The presence of ions in a liquid mixture increases the complexity of the system due to the superposition of long range electrostatic forces to the conventional short range interactions between the different species. The calculation of the vapour–liquid equilibrium (VLE) of such complex systems by means of group contribution g^E-models, e.g. Achard et al. [1,2], is a promising approach. The thermodynamic consistency of the model can be improved by fitting the model parameters to both, VLE- and h^E-data. While VLE-data of electrolyte systems can quite often be found in literature, there are less excess enthalpy data available for liquid mixtures including salt, e.g. [3–6]. Initialized by the Deutsche Forschungsgemeinschaft, we started measuring excess enthalpies of liquid mixtures containing cyclic, aromatic, alcohol- or water-functional groups under the influence of sodium chloride using a flow calorimeter. The subject of this paper is the description of the measuring apparatus including the flow-mix cell. Furthermore, first results are presented, mainly for 298.15 K.

2. Experimental

2.1. Purity of material

Prior to use, methanol (Roth; analytical grade 99.9%), ethanol (Roth; analytical grade 99.8%), benzylalcohol (Fluka; analytical grade 99.0%), and cyclohexane (Fluka; analytical grade 99.8%) were dried using beads of molecular sieve (Dehydrate Fluka). Water was distilled four times and all sample liquids were partially degassed under vacuum. Sodium chloride (Merck, puriss.) was dried at 220°C under vacuum before use.

---

*Corresponding author. Fax: 00 49 2317552572.

[1] Presented at the Twelfth Ulm-Freiberg Conference, Freiberg, Germany, 19–21 March 1997

PII S0040-6031(97)00386-9

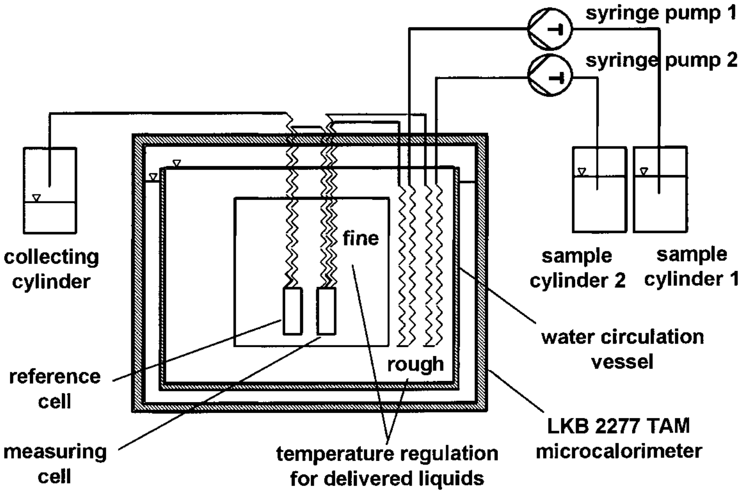

Fig. 1. Experimental setup of the microcalorimetric measuring devices.

2.2. Calorimetry

The excess enthalpy measurements were carried out using an LKB 2277 microcalorimeter which is illustrated schematically in Fig. 1. Due to the corrosive electrolyte solutions, the common flow-mix cell consisting of stainless steel capillary pipes could not be used. Therefore, the following experimental setup was developed.

The salt is dissolved a priori in the more polar of the two liquids to be mixed. The electrolyte solution and the pure, less polar liquid are pumped into the calorimeter through PTFE-tubes (0.8 mm inner diameter) using microliter syringes which are controlled by a stepping motor. A rough temperature regulation is achieved by leading approximately 2.5 m of tubing through the water circulation vessel of the calorimeter. Thus, the measuring temperature is attained and maintained constant to ±0.001 K. The fine tuning of the temperature of the sample fluids takes place inside the measuring shaft of the calorimeter on the way down to the measuring cell. For this purpose, about 3 m of both inlet tubes as well as 3 m of the outlet tube are wound up and twisted against each other to form a counter current heat exchanger. Its performance is supported by the surrounding water circulation vessel which is maintained at constant temperature. The two sample liquids are mixed in the measuring cell. Afterwards, the mixture is pumped through the reference cell in order to take advantage of the twin measuring principle and is finally delivered into the collecting cylinder.

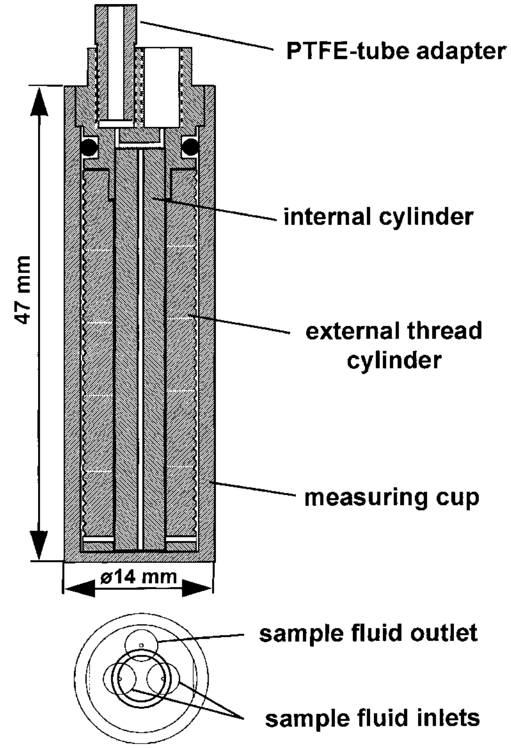

Fig. 2. Measuring cell.

Fig. 2 displays a more detailed view of the measuring cell. In order to resist the corrosion attack represented by the electrolyte solutions, the measuring cell and the reference cell are made of Hastelloy. The two sample liquids are mixed at the top of the measuring cell. The mixture passes the external thread of two cylinders which are fitted into each other. Due to the low pitch of the thread, the retention time inside the cell is rather high being between 0.5 and 4 min depending on the flow rate of the sample fluids of 0.001 to 0.6 ml/min.

3. Results and discussion

The results of the effect of NaCl on the excess molar enthalpy of the examined liquid mixtures are given in Table 1. The excess enthalpy of the ternary system, h^E_{123}, is calculated using Eq. (1):

$$h^E_{123} = h^E_{1+23} + (1 - x_1)\tilde{x}_3(h^{\text{int}}_s - h^{\text{int},\infty}_s). \qquad (1)$$

It refers to the mixture of solvent (1) with solvent (2) and the solute (3) with the standard state of the latter being the electrolyte at infinite dilution. The tilde indicates the binary system consisting of salt (3) and solvent (2). Thus, $\tilde{x}_3$ corresponds to the mole fraction of salt (3) in the binary system only. The integral molar enthalpy of solution, h^{int}_s, at the concentration $\tilde{x}_3$ and the molar enthalpy of solution at infinite dilution, $h^{\text{int},\infty}_s$, are given in J/mol solute and, for water as a solvent, are taken from Ref. [7]. There are no data available for the solution enthalpies of NaCl in methanol for different salt concentrations. However, due to the small solubility of NaCl in this organic solvent, only a slight difference between h^E_{1+23} and h^E_{123} is to be expected.

Table 2 gives the measured excess molar enthalpies of the binary liquid mixtures without salt. In Table 3, the coefficients for the Redlich–Kister polynomial,

$$h^E_{1+23} = \frac{x_1(1 - x_1)\sum_i B_i(2x_1 - 1)^{i-1}}{1 + k(2x_1 - 1)}, \qquad (2)$$

are given for the electrolyte systems without miscibility gap.

Fig. 3–6 show the excess isotherms of the systems in question. The calorimeter and the experimental setup, respectively, were tested with the ethanol+(water+NaCl) reference system for which data are available from literature. The data given by Benson et al. [3] for 298.15 K and for a 1 M solution of NaCl in water were also measured using a flow calorimeter. The deviations between our results and the data from Benson et al. [3] are about 2% and are of the same order of magnitude as the deviations between our measured excess enthalpies for the system without salt and the corresponding reference data (Boyne et al. [8]).

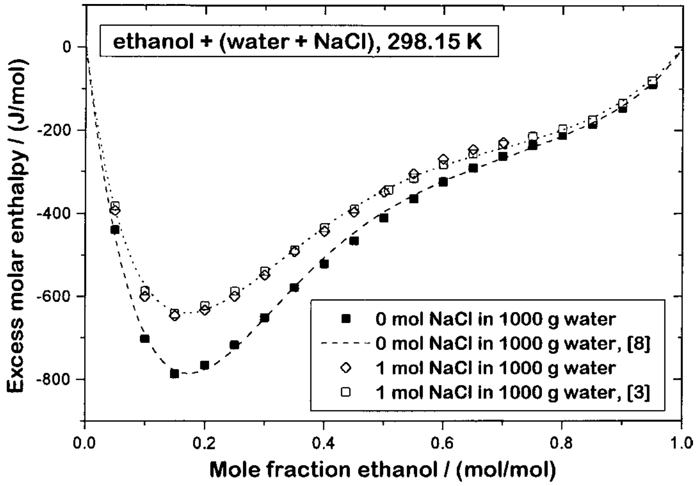

Fig. 3. Excess molar enthalpies h^E_{1+2} and h^E_{1+23} of ethanol (1)+water (2)+NaCl (3).

Table 1
Experimental (h^E_{1+23}) and calculated (h^E_{123}) excess molar enthalpies at different NaCl concentrations

x_1	h^E_{1+23} (J/mol)	h^E_{123} (J/mol)	x_1	h^E_{1+23} (J/mol)	h^E_{123} (J/mol)
Methanol (1)+water (2)+NaCl (3), $\tilde{w}_3 = 0.05$, T=298.15 K					
0.050	−289.07	−289.38	0.500	−744.97	−745.13
0.100	−515.76	−516.05	0.550	−709.42	−709.57
0.150	−665.18	−665.46	0.600	−673.92	−674.05
0.200	−753.40	−753.66	0.650	−629.52	−629.63
0.250	−801.63	−801.88	0.700	−557.13	−557.23
0.300	−823.33	−823.56	0.750	−517.82	−517.90
0.350	−808.35	−808.56	0.799	−438.24	−438.31
0.400	−788.92	−789.12	0.851	−361.73	−361.78
0.450	−766.12	−766.30	0.900	−257.60	−257.63
Methanol (1)+water (2)+NaCl (3), $\tilde{w}_3 = 0.10$, T=298.15 K					
0.050	−252.01	−273.31	0.500	−683.75	−694.96
0.100	−469.84	−490.01	0.550	−659.68	−669.77
0.150	−609.49	−628.54	0.600	−631.40	−640.37
0.200	−688.94	−706.87	0.650	−595.47	−603.32
0.250	−712.08	−728.89	0.700	−554.77	−561.50
0.300	−738.06	−753.75	0.750	−489.22	−494.82
0.350	−726.24	−740.81	0.800	−438.35	−442.83
0.400	−716.92	−730.37	0.850	−358.98	−362.34
0.450	−704.56	−716.89	0.900	−259.89	−262.13
Methanol (1)+water (2)+NaCl (3), $\tilde{w}_3 = 0.05$, T=323.15 K					
0.050	−137.35	−123.51	0.500	−615.62	−608.34
0.100	−394.37	−381.26	0.550	−592.21	−585.66
0.150	−505.70	−493.32	0.600	−568.38	−562.55
0.200	−585.01	−573.36	0.650	−536.21	−531.11
0.250	−626.04	−615.12	0.700	−498.07	−493.70
0.300	−646.95	−636.75	0.750	−448.53	−444.89
0.350	−650.71	−641.24	0.799	−392.34	−389.41
0.400	−638.83	−630.09	0.849	−320.83	−318.63
0.450	−631.09	−623.08	0.900	−232.00	−230.54
Methanol (1)+water (2)+NaCl (3), $\tilde{w}_3 = 0.10$, T=323.15 K					
0.050	−202.82	−177.87	0.500	−562.40	−549.27
0.100	−351.61	−327.97	0.550	−547.74	−535.92
0.150	−447.44	−425.11	0.600	−528.24	−517.74
0.200	−522.35	−501.34	0.650	−503.97	−494.77
0.250	−558.14	−538.44	0.700	−474.85	−466.97
0.300	−571.22	−552.83	0.750	−437.03	−430.47
0.350	−579.21	−562.13	0.800	−384.84	−379.57
0.400	−581.60	−565.84	0.850	−318.60	−314.65
0.450	−573.12	−558.67	0.900	−227.76	−225.15
Ethanol (1)+water (2)+NaCl (3), $\tilde{w}_3 = 0.0553$, T=298.15 K					
0.050	−392.88	−397.55	0.400	−442.39	−445.34
0.100	−600.54	−604.97	0.450	−397.01	−399.71
0.150	−646.57	−650.75	0.500	−348.02	−350.48
0.200	−633.01	−636.95	0.550	−303.89	−306.10
0.250	−599.52	−603.21	0.600	−268.41	−270.38
0.300	−548.19	−551.64	0.650	−245.78	−247.51
0.350	−491.70	−494.90	0.700	−229.73	−231.20

Table 1
(Continued)

x_1	h^{E}_{1+23} (J/mol)	h^{E}_{123} (J/mol)	x_1	h^{E}_{1+23} (J/mol)	h^{E}_{123} (J/mol)
Benzylalcohol (1)+water (2)+NaCl (3), $\tilde{w}_3 = 0.05$, T=298.15 K					
0.050	71.71	71.40	0.500	625.18	625.01
0.100	141.04	140.74	0.549	669.71	669.56
0.150	209.09	208.81	0.600	735.60	735.47
0.200	276.37	276.11	0.650	756.06	755.95
0.250	343.93	343.68	0.680	766.69	766.58
0.300	406.86	406.63	0.709	749.85	749.75
0.350	470.50	470.28	0.740	715.80	715.71
0.400	523.96	523.76	0.770	670.64	670.57
0.449	578.29	578.11			
Benzylalcohol (1)+water (2)+NaCl (3), $\tilde{w}_3 = 0.10$, T=298.15 K					
0.050	66.19	44.90	0.400	466.47	453.01
0.100	127.75	107.58	0.450	513.22	500.89
0.150	184.17	165.12	0.501	550.64	539.45
0.200	249.03	231.10	0.550	514.02	503.93
0.250	308.22	291.42	0.561	613.50	603.66
0.300	364.38	348.69	0.590	628.78	619.59
0.350	417.40	402.84	0.620	649.42	640.91
Cyclohexane (1)+methanol (2)+NaCl (3), $\tilde{w}_3 = 0.002$, T=298.15 K					
0.350	477.07		0.170	476.16	
0.330	473.38		0.150	469.20	
0.310	470.54		0.130	436.21	
0.290	479.51		0.110	387.90	
0.270	479.54		0.090	337.90	
0.250	483.50		0.070	276.41	
0.230	484.27		0.050	208.02	
0.210	487.75		0.030	131.04	
0.190	486.98				
Cyclohexane (1)+methanol (2)+NaCl (3), $\tilde{w}_3 = 0.004$, T=298.15 K					
0.100	362.46		0.050	209.48	
0.090	347.45		0.040	171.18	
0.080	301.48		0.030	131.91	
0.070	277.08		0.020	89.04	
0.060	248.03				
Cyclohexane (1)+methanol (2)+NaCl (3), $\tilde{w}_3 = 0.008$, T=298.15 K					
0.100	353.57		0.030	128.96	
0.040	154.59		0.020	86.83	

In Fig. 4, our experimental data for the methanol+(water+NaCl) system for two temperatures as well as the corresponding Redlich–Kister fit curves are displayed. The deviations between the experimental data and the data calculated using the Redlich–Kister parameters are less than 2%.

Figs. 5 and 6 show systems having a miscibility gap at 298.15 K. Due to the limited solubility of sodium chloride in the organic solvents, the isotherms cannot be measured over the entire concentration range but only up to approximately saturation conditions. In order to avoid the risk of blocking the tubes of the

Table 2
Experimental (h^{E}_{1+2}) excess molar enthalpies for binary liquid mixtures without salt

x_1	h^{E}_{1+2} (J/mol)	x_1	h^{E}_{1+2} (J/mol)	x_1	h^{E}_{1+2} (J/mol)
Ethanol (1)+water (2), T=298.15 K					
0.050	−439.40	0.400	−521.37	0.700	−262.82
0.100	−701.99	0.450	−465.52	0.750	−236.68
0.150	−787.05	0.500	−410.87	0.800	−212.98
0.200	−765.02	0.550	−364.48	0.850	−184.95
0.250	−717.29	0.600	−324.03	0.900	−146.15
0.300	−651.79	0.650	−291.13	0.950	−89.67
0.350	−578.13				
Benzylalcohol (1)+water (2), T=298.15 K					
0.050	74.03	0.450	671.61	0.800	666.60
0.100	149.71	0.500	671.61	0.830	591.21
0.150	226.89	0.550	732.93	0.860	510.35
0.200	303.76	0.650	839.76	0.890	405.19
0.250	377.26	0.680	854.46	0.920	296.65
0.300	431.84	0.710	832.76	0.950	194.13
0.350	509.38	0.740	798.23	0.980	76.21
0.400	580.27	0.770	735.21		
Cyclohexane (1)+methanol (2), T=298.15 K					
0.985	181.07	0.840	426.66	0.160	494.93
0.975	230.77	0.830	427.06	0.150	474.77
0.950	301.74	0.751	445.10	0.140	457.82
0.930	338.99	0.650	459.16	0.130	433.86
0.920	355.42	0.550	471.45	0.120	414.59
0.910	370.64	0.450	483.47	0.100	364.85
0.900	380.03	0.350	495.56	0.080	309.70
0.890	387.63	0.250	507.00	0.060	247.09
0.880	405.57	0.230	509.92	0.046	196.05
0.870	414.13	0.190	512.49	0.040	173.76
0.860	416.91	0.180	511.42	0.028	124.44
0.850	420.92	0.170	506.86		

Table 3
Redlich–Kister coefficients for electrolyte systems without miscibility gap

$\tilde{w}_3$	B_0	B_1	B_2	k
Methanol (1)+water (2)+NaCl (3), T=298.15 K				
0.05	−2971.79	545.46	−1630.56	0.281
0.10	−2735.58	188.60	−1671.22	0.302
Methanol (1)+water (2)+NaCl (3), T=323.15 K				
0.05	−2474.53	925.05	−1462.15	0.001
0.10	−2251.97	−77.28	−1353.77	0.272
Ethanol (1)+water (2)+NaCl (3), T=298.15 K				
0.0553	−1373.92	581.16	−1932.62	0.646

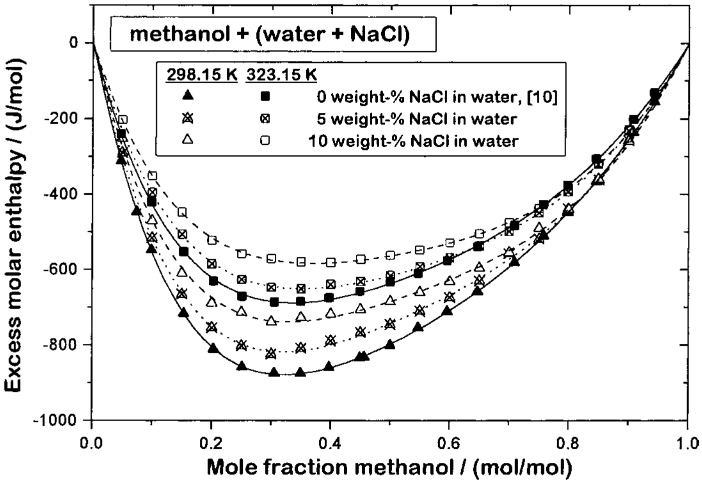

Fig. 4. Excess molar enthalpies h^E_{1+2} and h^E_{1+23} of methanol (1)+water (2)+NaCl (3) Ref. [10]: 0 weight.% NaCl in water.

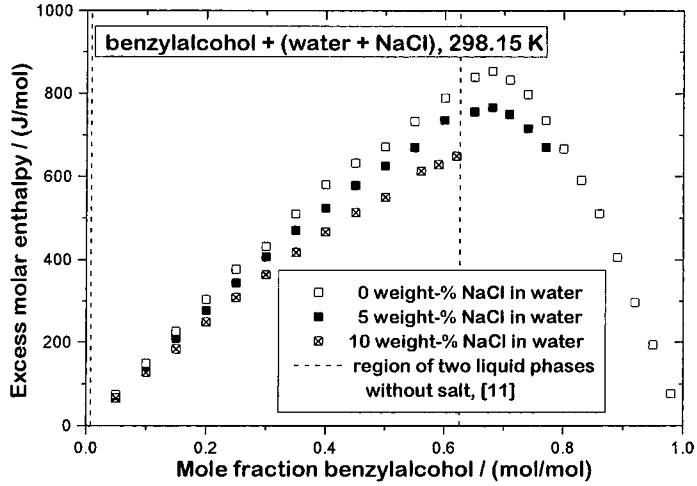

Fig. 5. Excess molar enthalpies h^E_{1+2} and h^E_{1+23} of benzylalcohol (1)+water (2)+NaCl (3) Ref. [11]: without salt.

flow-mix setup due to crystallization, the saturation point in the ternary systems (two solvents plus salt) was investigated as reported elsewhere [9] before the excess enthalpy measurements were carried out.

The concentration range available for calorimetric measurements decreases as the organic solvents become more non-polar. Whereas, in the system methanol+(water+NaCl), system concentrations up to 95 mol% methanol are possible for 5 and 10 wt% NaCl in water, respectively, excess enthalpy measurements for benzylalcohol+(water+NaCl) can only be carried out up to about 77 and 62 mol% benzylalcohol using aqueous solutions of 5 and 10 wt% NaCl, respectively. In the cyclohexane+(methanol+NaCl) system, both solvents are organic liquids. Thus, the solubility of NaCl in the binary solvent mixture is much lower over the entire concentration range. In pure cyclohexane, the solubility tends towards zero. Apart from limiting the absolute salt concentration in the more polar of the two sample fluids, the above mentioned circumstance requires much smaller steps in the variation of the salt concentration (0.2, 0.4, and 0.8 wt% NaCl in water) whereas in aqueous mixtures, the salt concentration can be varied in steps of 5 wt%.

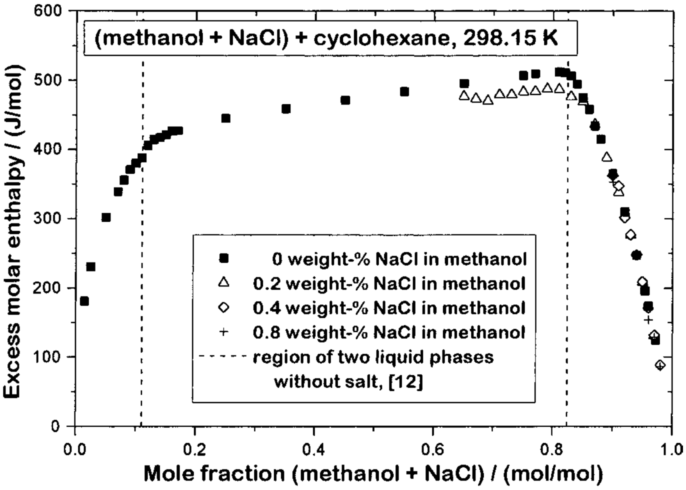

Fig. 6. Excess molar enthalpies h^E_{1+2} and h^E_{1+23} of cyclohexane (1)+methanol (2)+NaCl (3) Ref. [12]: without salt.

Due to the limited salt concentration and the small concentration differences for different measurements, the excess molar enthalpies of cyclohexane+(methanol+NaCl) do not vary much. Only in the region where two liquid phases exist, a slight effect can be observed which indicates a shift of the border of the miscibility gap to lower mole fractions of cyclohexane as reported in [13]. However, at least for 298.15 K, the shift cannot be quantified using the current microcalorimetric setup. Near the critical solution temperature of about 316 K, however, the effect of the addition of salt on the position of the miscibility gap is higher [13] and greater enthalpic effects might be measured, as well.

Generally speaking, for all investigated systems, the absolute value of the excess molar enthalpy decreases with increasing concentrations of NaCl, i.e. exothermal or endothermal behaviour, respectively, is reduced by the influence of the added electrolyte.

Acknowledgements

The authors thank the DFG (Deutsche Forschungsgemeinschaft) for the financial aid which supported these studies.

References

[1] C. Achard, C.G. Dussap, J.B. Gros, Fluid Phase Equilibria 98 (1994) 71.
[2] C. Achard, C.G. Dussap, J.B. Gros, AIChE Journal 40 (1994) 1210.
[3] G.C. Benson, E. Zhao, B.C.-Y. Lu, J. Chem. Eng. Data 40 (1995) 665.
[4] M. Rajendran, S. Renganarayanan, P.R. Madhavan, D. Srinivasan, Chem. Eng. Comm. 74 (1988) 179.
[5] M. Rajendran, S. Renganarayanan, D. Srinivasan, Fluid Phase Equilibria 70 (1991) 65–106.
[6] M. Rajendran, D. Srinivasan, Chem. Eng. Comm. 128 (1994) 109–117.
[7] E.C.W. Clarke, D.N. Glew, J. Phys. Chem. Ref. Data 14 (1985) 489.
[8] J.A. Boyne, A.G. Williamson, J. Chem. Eng. Data 12 (1967) 318.
[9] K. Wagner, T. Friese, S. Schulz, P. Ulbig, submitted for publication to J. Chem. Eng. Data.
[10] B. Löwen, PhD Thesis, Universität Dortmund, Verlag Shaker Aachen (1995).
[11] R. Stephenson, J. Stuart, J. Chem. Eng. Data 31 (1986) 56.
[12] J.M. Sørensen, W. Arlt, Dechema Data Series 5 (1979).
[13] E.L. Eckfeldt, W.W. Lucasse, J. Phys. Chem. 21 (1943) 164.