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Excess Enthalpies of (*N*-Methylformamide or *N*-Methylacetamide) + Aromatic Compounds at 303.15 K

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The excess molar enthalpies, H_m^E, of (*N*-methylformamide or *N*-methylacetamide + benzene, or + toluene, *p*-xylene, or mesitylene) at 303.15 K have been determined experimentally as a function of mole fraction. H_m^E shows partial miscibility for the system *N*-methylformamide + *p*-xylene. H_m^E is positive for all the mixtures.

1. Introduction

Amides, amino acids, peptides, and their derivatives are of interest because they are simple models in biochemistry. *N*-Methylformamide possesses the basic (−CO) and acidic (−NH) groups of the very common, in nature, peptide bond.[1] Consequently, the understanding of liquid mixtures involving the amide functional group is necessary as a first step to a better knowledge of complex molecules of biological interest.[2–4] For example, the aqueous solution of *N*,*N*-dimethylformamide is a model solvent representing the environment of the interior of proteins. Moreover, *N*,*N*-dimethylformamide and *N*-methylpropanamide are used as highly selective extractants for the recovery of aromatic and saturated hydrocarbons from petroleum feedstocks.[1] From a theoretical point of view, amides are also a very interesting class of compounds. In the pure liquid state, they present a significant local order as their quite high enthalpies of vaporization, $\Delta_{vap}H$, indicate. In the case of amides and *N*-alkylamides, this is due to the dipole–dipole interactions, but also their self-association via H-bonds must be taken into account. On the other hand, mixtures containing a polar component of high polarity such as *N*-methylpropanamide and alkanes of benzene are located on the G^E-H^E diagram in a range between hydrogen bond associated and nonassociated mixtures.[1]

We present here the experimental excess molar enthalpies H_m^E for [(*x*) {$HCONCH_3H$ or CH_3CONCH_3H} + (1−*x*) {C_6H_6 or $C_6H_5CH_3$ or 1,4-$C_6H_4(CH_3)_2$ or 1,3,5-$C_6H_3(CH_3)_3$} at 303.15 K]. The previous calorimetric studies on these mixtures are those of Becker[5] on (*N*-methylformamide + benzene or + toluene) at 298.15 K with values of 414.5 J·mol^{-1} and 451.5 J·mol^{-1}, respectively, for H_m^E at equimolar composition, those of Messow et al.[6] on (*N*-methylformamide + benzene) at (298.15 and 318.15) K with values of 385.5 J·mol^{-1} and 442.8 J·mol^{-1}, respectively, for H_m^E at equimolar composition, and those from de Haan and Gmehling[7] on (*N*-methylacetamide + benzene or toluene) at 363.15 K with values of 402.1 J·mol^{-1} and 507.5 J·mol^{-1}, respectively, for H_m^E at equimolar composition. From the comparison with data from the literature, it can be said that our data follow the right trend. As far as we know, there are no calorimetric studies on the other systems.

Table 1. Experimental Excess Molar Enthalpies H_m^E for the Studied Mixtures at 303.15 K

x	H_m^E / J·mol^{-1}	*x*	H_m^E / J·mol^{-1}	*x*	H_m^E / J·mol^{-1}
N-Methylformamide (*x*) + Benzene (1−*x*)					
0.0011	11	0.3412	416	0.6012	350
0.0019	19	0.3720	423	0.6365	333
0.1401	339	0.4280	417	0.7237	272
0.2247	384	0.4525	409	0.8274	178
0.2851	405	0.5333	388		
N-Methylformamide (*x*) + Toluene (1−*x*)					
0.1531	408	0.3983	483	0.6171	426
0.1852	425	0.4643	484	0.6450	402
0.2625	461	0.4821	475	0.7416	320
0.3018	467	0.5253	459	0.8178	240
0.3404	482	0.5951	432	0.9166	127
N-Methylformamide (*x*) + *p*-Xylene (1−*x*)					
0.0589	291	0.3545	463	0.7042	440
0.0809	330	0.4435	484	0.7619	381
0.1371	439	0.5245	516	0.8196	302
0.2251	449	0.6034	511	0.8715	223
0.2742	452	0.6480	489	0.9536	101
N-Methylacetamide (*x*) + Benzene (1−*x*)					
0.0848	214	0.4282	194	0.6331	123
0.1579	235	0.4628	176	0.7660	72
0.2196	241	0.4950	164	0.8432	52
0.2809	236	0.5438	144	0.8931	35
0.3924	216	0.5670	140		
N-Methylacetamide (*x*) + Toluene (1−*x*)					
0.1142	259	0.4365	200	0.7076	106
0.2405	259	0.4708	185	0.7798	75
0.2954	239	0.5227	179	0.9016	31
0.3770	221	0.5843	163		
0.4002	218	0.6502	126		
N-Methylacetamide (*x*) + *p*-Xylene (1−*x*)					
0.1224	279	0.4018	284	0.7529	153
0.1703	291	0.4704	261	0.8617	83
0.2407	295	0.6138	215		
0.3474	295	0.7126	168		
N-Methylacetamide (*x*) + Mesitylene (1−*x*)					
0.1463	342	0.4989	437	0.8071	254
0.2448	388	0.5612	409	0.8840	176
0.3271	429	0.6649	350		
0.4098	439	0.7283	317		

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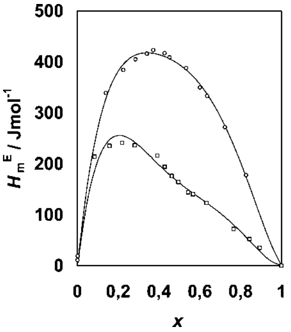

Figure 1. Experimental values (symbol) and calculations with eq 1 (line) for excess molar enthalpies H_m^E of: ○, *N*-methylformamide + (1−*x*) benzene; and □, *N*-methylacetamide + (1−*x*) benzene at 303.15 K.

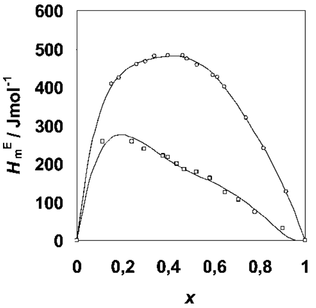

Figure 2. Experimental values (symbol) and calculations with eq 1 (line) for excess molar enthalpies H_m^E of: ○, *N*-methylformamide + (1−*x*) toluene; and □, *N*-methylacetamide + (1−*x*) toluene at 303.15 K.

2. Experimental Section

N-Methylformamide (mole fraction purity > 99 %) was obtained from Aldrich. *N*-Methylacetamide (mole fraction purity > 99 %), benzene (mole fraction purity > 99.7 %), toluene (mole fraction purity > 99.7 %), *p*-xylene (mole fraction purity > 99 %), and mesitylene (mole fraction purity > 98.5 %) were obtained from Merck. All the liquids were subjected to glc analysis and were used directly without further purification.

Excess enthalpies were measured with a quasi-isothermal calorimeter working at constant pressure in the absence of a vapor phase.[8] The uncertainty of the reported excess enthalpies was estimated to be less than 2 %. The mixtures were prepared by mass using a balance from Mettler with an uncertainty of ± 0.1 mg, and the mole fraction uncertainty was estimated to be less than $\pm\ 10^{-4}$. The temperature in the water bath was controlled to within 0.002 K, and the temperature uncertainty was estimated to be less than ± 0.01 K.

3. Results and Discussion

The values of H_m^E for the studied mixtures are listed in Table 1 and plotted against *x* in Figures 1 to 4. Each set of results was fitted by least-squares to a polynomial

$$H_m^E/(\mathrm{J\cdot mol^{-1}}) = x(1-x)\sum_{i=0}^{n} A_i(2x-1)^i \qquad (1)$$

These parameters appear with the standard deviations in Table 2.

N-Methylformamide + *p*-xylene show partial miscibility at the studied temperature, and the H_m^E values obtained in the region of total miscibility are positive. This behavior has been explained through dipolar interactions, additional or alternative to hydrogen bonding.[9]

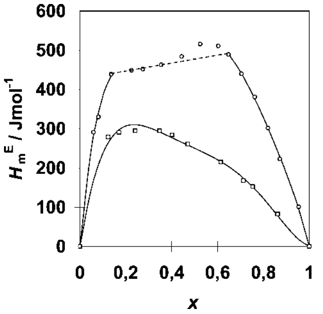

Figure 3. Experimental values (symbol) and calculations with eq 1 (line) for excess molar enthalpies H_m^E of: ○, *N*-methylformamide + (1−*x*) *p*-xylene; and □, *N*-methylacetamide + (1−*x*) *p*-xylene at 303.15 K.

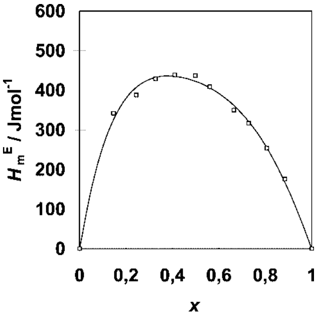

Figure 4. Experimental values (symbol) and calculations with eq 1 (line) for excess molar enthalpies H_m^E of: □, *N*-methylacetamide + (1−*x*) mesitylene at 303.15 K.

Table 2. Parameters A_i and Standard Deviations σ for Least-Squares Representations of H_m^E for Studied Mixtures by Equation 1

	A_0	A_1	A_2	A_3	A_4	σ/J·mol^{-1}
N-methylformamide + (1−*x*) benzene	1578	564.2	684.2	1020		8
N-methylformamide + (1−*x*) toluene	1891	469.8	268.8	1272	1482	4
N-methylformamide + (1−*x*) *p*-xylene[a]	2182	−30.9	176.1	−2088	2117	9
N-methylacetamide + (1−*x*) benzene	649.4	−640.5	994.7	−948.3		12
N-methylacetamide + (1−*x*) toluene	708.6	−574.4	1044.3	−1382.6		11
N-methylacetamide + (1−*x*) *p*-xylene	1001	−540.2	942.7	−1172		10
N-methylacetamide + (1−*x*) mesitylene	1690	−434.2	866.3	−508.1		13

[a] Parameters fitted for 0.1371 < *x* < 0.6480.

H_m^E values of (*N*-methylformamide or *N*-methylacetamide) + (benzene, or toluene, or *p*-xylene, or mesitylene) show an endothermic effect relative to *N*,*N*-dimethylformamide or *N*,*N*-dimethylacetamide mixtures.[10] This can be due to the existence of hydrogen bonding in the *N*-alkylamides. (*N*-Methylformamide + an aromatic hydrocarbon) give H_m^E between 394 J·mol^{-1} and 545 J·mol^{-1} at the maximum, greater than that for the corresponding (*N*-methylacetamide + an aromatic hydrocarbon). The H_m^E values of (*N*-methylformamide or *N*-methylacetamide + an aromatic hydrocarbon) increase with increasing number of methyl groups in the aromatic ring. Some measurements were carried out at 313.15 K to obtain the temperature coefficients $(\partial H_m^E/\partial T)_P$ for these mixtures at equimolar composition. The values obtained are positive: about 5.5 J·mol^{-1}·K^{-1} for *N*-methylformamide mixtures and 4.9 J·mol^{-1}·K^{-1} for the corresponding *N*-methylacetamide containing systems. These high values are in agreement with the importance of hydrogen bonding in the investigated solutions.

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