Enthalpies of Dilution and Enthalpic Interaction Coefficients of Several Substituted Amides Dissolved in *N*-Methylformamide

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Enthalpies of dilution of *N*-butylformamide, *N*-pentylformamide, *N*-methylacetamide, *N*-ethylacetamide, *N*-propylacetamide, *N*-butylacetamide, *N*,*N*-dimethylformamide, *N*,*N*-diethylformamide, *N*,*N*-dibutylformamide, *N*,*N*-dimethylacetamide, *N*,*N*-diethylacetamide, *N*,*N*-dipropylacetamide, *N*,*N*-dibutylacetamide, and *N*,*N*-dipentylacetamide dissolved in the protic solvent *N*-methylformamide have been measured microcalorimetrically at 298.15 K. From the results enthalpic interaction coefficients of the solutes have been calculated and these are compared with earlier results in the aprotic solvent dimethylformamide.

Introduction

This paper is part of a project in which we are investigating interactions of solutes in nonaqueous solvents. A thermodynamic way to explore these interactions in dilute solutions is by determining thermodynamic interaction coefficients. When the concentration dependence of a thermodynamic property of a dilute solution is expressed as a power series in the molality, it has been shown (*1*-*4*) that the n-th virial coefficient can be related to the solvent-mediated interaction of n solute molecules. These virial coefficients (also called interaction coefficients) are related to the cluster integrals in the McMillan–Mayer theory (*4*, *5*) and to the McMillan–Mayer coefficients (*6*). We have shown before (*4*) that, for the systems studied here, the effect of conversion from the McMillan–Mayer standard state (independent variables c, T, V) to the Lewis–Randall standard state (independent variables m, T, p) is negligible. In our project we focus attention to the enthalpies. Enthalpic interaction coefficients can be calculated from known excess enthalpies of binary mixtures (*7*) and obtained experimentally from enthalpies of dilution measured with a microcalorimeter (*8*). An extensive set of enthalpic interaction coefficients in the aprotic solvent *N*,*N*-dimethylformamide (DMF), determined by microcalorimetry, has been presented by us in recent years (*4*, *9*-*13*).

A subsequent step in our project is to choose *N*-methylformamide (NMF) as the solvent. Although the molecules of NMF differ from those of DMF in one CH_3 group being replaced by a H atom only, its solvent properties are quite different. It is a protic solvent with a high dielectric constant, reflecting a much more structured liquid state than present in DMF (*14*). In this paper we present enthalpies of dilution in NMF and enthalpic interaction coefficients calculated from these enthalpies for several alkyl-substituted formamides and acetamides, viz., *N*-butylformamide (NBF), *N*-pentylformamide (NPeF), *N*-methylacetamide (NMA), *N*-ethylacetamide (NEA), *N*-propylacetamide (NPrA), *N*-butylacetamide (NBA), *N*,*N*-dimethylformamide (DMF), *N*,*N*-diethylformamide (DEF), *N*,*N*-dibutylformamide (DBF), *N*,*N*-dimethylacetamide (DMA), *N*,*N*-diethylacetamide (DEA), *N*,*N*-dipropylacetamide (DPrA), *N*,*N*-dibutylacetamide (DBA), and *N*,*N*-dipentylacetamide (DPeA).

Experimental Section

Enthalpies of dilution were determined with a LKB 10700-2 batch microcalorimetric system. The output signal of the measuring cell was amplified by means of a Keathly 150B microvoltmeter and integrated by using a Kipp BD12 integrating recorder. Details of the experimental procedure have been described earlier (*4*, *9*, *15*). In order to speed the measurements, the method of subsequent dilutions (*9*, *15*, *16*) was used, in which after the first dilution experiment a maximal and known mass of solution in one of the compartments is replaced by a known mass of pure solvent. Thus, in the second experiment a solution is mixed with a highly diluted solution of the same kind. Due to the instability of NMF, generally only one subsequent dilution could be performed without introducing large deviations.

Synthesis and further details of the solutes have been published (*4*, *9*, *12*, *13*). The solvent NMF (Merck, z.Synthese) was purified according to the procedure of Verhoek (*17*) and always used within 24 h after distillation. The purity of NMF was tested by GLC analysis (column packed with 0.5% Na_3PO_4, 5% Polyglycol 1000 on Chromosorb GAW, 80–100 mesh), by Karl Fischer titration with regard to its water content (*18*), and by conductivity measurements in order to detect formic acid. The purity appeared to be at least 99.7 mass %.

Results and Discussion

A compilation of the dilution experiments is given in Table I, which presents the enthalpy change, ΔH, when n_A moles of solute at molality $m_{A,i}$ are mixed with n_B moles of solute at molality $m_{B,i}$ (or with pure NMF, $n_B = 0$ mol, $m_{B,i} = 0$ mol kg^{-1}) to give a solution with final molality m_f. If $H^E(m)$ denotes the excess enthalpy of a solution per mole of solute at molality m, ΔH can be written as

$$\Delta H = n_A[H^E(m_f) - H^E(m_{A,i})] + n_B[H^E(m_f) - H^E(m_{B,i})] \quad (1)$$

The molar excess enthalpy of a solution containing a single solute at molality m may be represented (*4*, *8*) by

$$H^E(m) = B_2^h m + B_3^h m^2 + \ldots \quad (2)$$

in which B_2^h, B_3^h, ... are virial coefficients representing pair, triplet, and higher interactions of the solute particles. Combination of eq 1 and eq 2 gives

$$\Delta H/n_A = \sum_{n>1} B_n^h[(m_f^{n-1} - m_{A,i}^{n-1}) + n_A^{-1} n_B (m_f^{n-1} - m_{B,i}^{n-1})] \quad (3)$$

The enthalpic interaction coefficients, B_n^h, have been calculated by a least-squares analysis of the results of Table I in terms of eq 3. Resulting values and their standard deviations are collected in Table II. It should be emphasized that the overall uncertainty in the values may be larger, due to impurities in the chemicals and systematic errors in the experiments. B_4^h was only used when the Student' t-test indicated a probability

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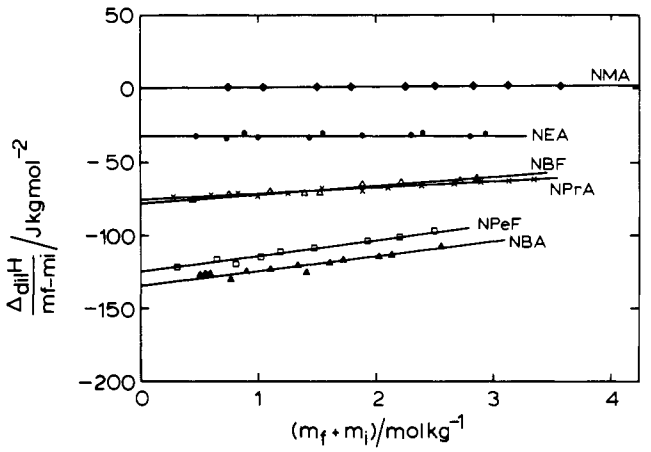

Figure 1. Enthalpies of dilution for some *N*-alkylamides dissolved in NMF.

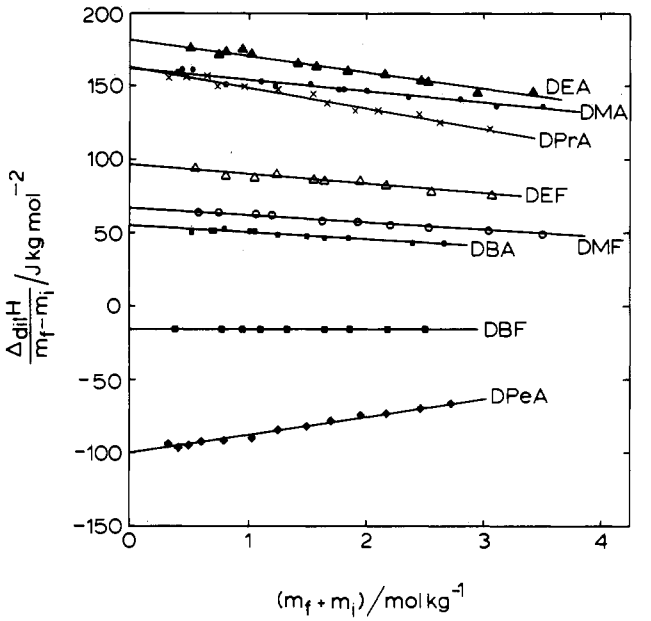

Figure 2. Enthalpies of dilution of some *N*,*N*-dialkylamides dissolved in NMF

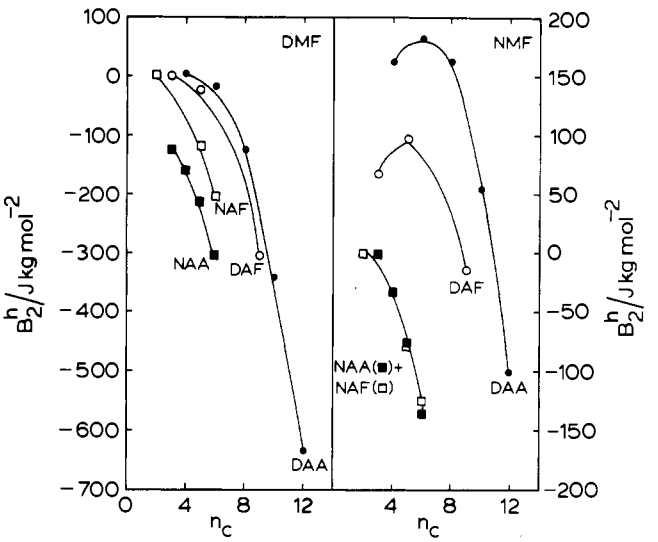

Figure 3. Enthalpic pair interaction coefficients of alkyl-substituted amides dissolved in DMF and NMF vs. the number of C atoms in the solute (NAF = *N*-alkylformamides; NAA = *N*-alkylacetamides; DAF = *N*,*N*-dialkylformamides; DAA = *N*,*N*-dialkylacetamides).

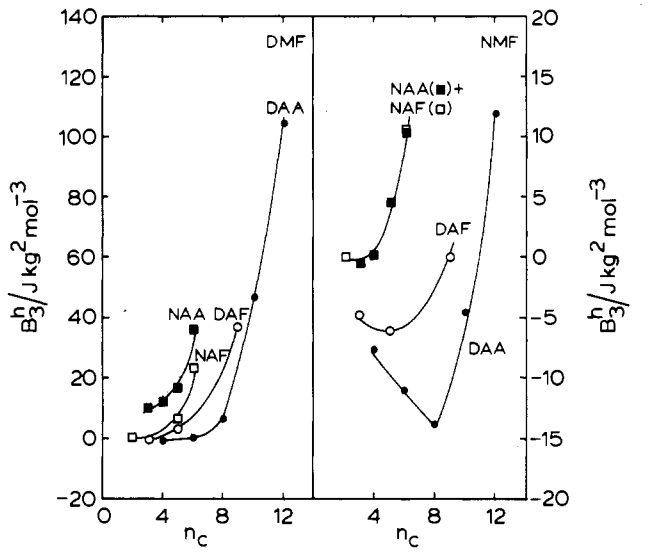

Figure 4. Enthalpic triplet coefficients of several substituted amides dissolved in DMF and NMF vs. the number of C atoms in the solute (compounds abbreviated as in Figure 3).

of more than 95% that its value was not zero. From eq 3 it follows that

$$\Delta_{dil}H(m_{A,i} \rightarrow m_f) = \Delta H/n_A - n_A^{-1} n_B \sum_{n>1} B_n^h (m_f^{n-1} - m_{B,i}^{n-1}) \quad (4)$$

where $\Delta_{dil}H(m_{A,i} \rightarrow m_f)$ is the enthalpy change per mole of solute on diluting a solution from initial molality $m_{A,i}$ to final molality m_f. Since

$$\Delta_{dil}H(m_i \rightarrow m_f)/(m_f - m_i) = B_2^h + B_3^h(m_f + m_i) + B_4^h(m_f^2 + m_i^2 + m_f m_i) + \ldots . \quad (5)$$

and B_4^h is small as compared to B_3^h, we give a graphical representation of the experimental results as $\Delta_{dil}H/(m_f - m_i)$ vs. $m_f + m_i$) with enthalpies of dilution calculated according to eq 4 in Figures 1 and 2. In these figures B_2^h and B_3^h are represented by the intercept and the (limiting) slope, respectively, of the curves.

In Figures 3 and 4 the enthalpic interaction coefficients in *N*-methylformamide, reported here, are compared with those of similar compounds in *N*,*N*-dimethylformamide published before (*4*, *9*, *12*). It appears that values of the interaction coefficients are of comparable magnitude in both solvents with pair coefficients shifted in a positive way and triplet coefficients in a negative direction when the values in NMF are compared with those in DMF. In addition, the variation in both B_2^h and B_3^h is smaller in the solvent NMF. The following general trends can be observed in both solvents. (a) Generally, the enthalpic pair interaction coefficients decrease and the triplet coefficients increase with increasing size of the alkyl groups of the solute molecules. (b) The values of B_2^h and B_3^h of one compound are always of opposite sign. (c) Values of B_2^h for dialkylamides are more positive than those of corresponding monoalkylamides, whereas their B_3^h values are less positive. (d) The values of B_2^h

Table I. Enthalpies of Dilution of Several Solutes Dissolved in NMF at 298.15 K

$m_{A,i}$, mol kg^{-1}	n_A, mmol	$m_{B,i}$, mmol kg^{-1}	n_B, μmol	m_f, mol kg^{-1}	ΔH, mJ	% Δ[a]	$m_{A,i}$, mol kg^{-1}	n_A, mmol	$m_{B,i}$, mmol kg^{-1}	n_B, μmol	m_f, mol kg^{-1}	ΔH, mJ	% Δ[a]
						N-Butylformamide							
0.3280	0.7253	0	0	0.1113	11.94	+0.5%	1.0854	4.4507	4.5	23.7	0.7946	83.99	−2.4%
0.6086	0.8860	3.2	13.5	0.1566	29.05	−1.1%	1.3641	4.9581	0	0	0.8390	170.27	−0.4%
0.8390	1.4740	4.4	18.2	0.2526	60.98	−1.3%	1.5838	5.7541	0	0	1.1079	173.39	+0.6%
0.9179	3.4793	0	0	0.6086	74.66	−0.1%	1.7791	6.3757	0	0	1.0854	275.05	+0.4%
1.1079	1.2613	6.8	23.5	0.2782	79.91	+2.4%							
						N-Pentylformamide							
0.2262	0.3985	1.2	5.2	0.0652	7.88	+1.0%	0.9521	1.2075	4.8	20.2	0.2245	96.75	−1.9%
0.4047	0.6672	2.1	9.1	0.1126	22.81	−1.9%	1.3645	4.6208	0	0	0.8551	240.05	+0.3%
0.6189	1.0938	0	0	0.1767	57.83	−2.2%	1.5436	5.0026	0	0	0.9521	288.06	−1.4%
0.8551	3.4935	12.3	18.8	0.6247	86.66	−0.2%	1.5436	2.4113	0	0	0.4047	289.35	+0.8%
0.7904	1.4007	0	0	0.2262	91.20	+0.8%							
						N-Methylacetamide							
0.7897	1.6225	0.6	2.5	0.2641	1.33	−0.5%	1.5359	5.4469	0	0	0.9822	6.66	+0.2%
0.8964	3.7311	9.9	21.0	0.5983	1.94	−0.4%	1.7388	6.0027	0	0	1.0928	9.03	−0.3%
1.0928	2.0184	0.8	3.5	0.3396	2.66	+1.0%	1.9311	6.7101	0	0	1.2006	12.25	+1.3%
1.3809	2.1904	7.6	29.6	0.4055	4.01	−0.3%	2.1909	7.7072	0	0	1.3809	16.51	−0.4%
1.3513	5.4703	14.7	30.6	0.8964	5.02	−0.4%							
						N-Ethylacetamide							
0.3658	0.5972	2.1	8.4	0.1077	4.86	−0.6%	1.4410	2.5582	0	0	0.4396	81.91	+0.1%
0.4396	1.8927	4.8	10.2	0.2963	8.83	+3.0%	1.4716	5.1364	0	0	0.9244	84.39	−6.2%
0.5286	2.3366	6.0	12.2	0.3584	11.38	−5.5%	1.7750	3.0302	0	0	0.5286	120.53	+0.0%
0.7596	1.4616	0	0	0.2452	24.79	+3.3%	1.7180	5.9690	0	0	1.0800	124.49	+2.4%
0.9244	3.8023	10.1	20.7	0.6199	35.11	−4.0%	1.8030	6.1798	0	0	1.1396	125.03	−4.8%
1.1396	1.6594	5.8	24.5	0.2984	45.85	+3.4%							
						N-Propylacetamide							
0.2406	0.3285	1.3	5.5	0.0574	4.41	−1.8%	1.2894	4.6984	13.7	27.5	0.8347	138.25	−0.9%
0.4886	0.6664	2.6	11.0	0.1202	17.83	−0.7%	1.9343	2.4078	0	0	0.4621	232.64	+0.2%
0.5057	1.8964	0	0	0.3314	24.15	+0.7%	1.7897	5.8322	0	0	1.1119	251.28	+0.5%
0.7554	2.7572	0	0	0.4886	52.79	+1.5%	1.9343	6.2901	0	0	1.2019	290.45	+1.4%
0.7554	1.3933	0	0	0.2406	53.54	+3.8%	2.0713	3.4007	0	0	0.6099	318.65	−0.2%
1.1119	4.5080	13.1	24.2	0.7684	107.54	+3.6%	2.0713	6.8895	0	0	1.2849	323.42	+0.5%
1.2019	1.9514	6.4	25.3	0.3534	112.26	−1.6%							
						N-Butylacetamide							
0.4468	0.2233	2.5	10.0	0.0518	11.16	−2.0%	0.9686	3.8449	10.0	21.1	0.6360	150.97	+0.6%
0.3445	1.4687	4.0	8.3	0.2327	20.51	−2.1%	1.0678	1.9063	0	0	0.3260	175.02	+2.4%
0.4201	0.8167	0	0	0.1378	29.05	−2.8%	1.0617	3.7053	0	0	0.6554	178.44	+0.9%
0.4603	1.9509	5.0	10.6	0.3089	37.90	+2.0%	1.3027	4.4405	0	0	0.8300	240.65	+1.2%
0.5365	2.0169	0	0	0.3445	49.16	+0.7%	1.5714	2.6019	0	0	0.4603	329.76	−0.2%
0.6554	2.6790	7.2	15.2	0.4356	72.42	+0.5%	1.5846	5.1937	0	0	0.9686	344.81	−1.1%
0.8300	2.0186	8.6	18.3	0.4468	91.93	−1.5%							
						N,*N*-Dimethylformamide							
0.7414	0.5542	2.5	10.6	0.1044	−13.08	+1.2%	1.1685	4.8933	11.7	26.0	0.7675	−109.97	−1.3%
0.4415	1.8598	0	0	0.3170	−14.77	+1.1%	1.3292	5.4936	13.0	29.3	0.8644	−138.38	−2.5%
0.6390	2.7740	6.5	14.8	0.4223	−37.55	+2.4%	1.5614	5.8485	0	0	0.9846	−183.24	−0.3%
0.3727	2.7792	0	0	0.4714	−45.45	+2.7%	1.8747	6.9767	0	0	1.1685	−258.17	+0.6%
0.9905	3.8438	0	0	0.6390	−78.61	−1.2%	2.1646	7.9761	0	0	1.3292	−334.23	+0.5%
						N,*N*-Diethylformamide							
0.4340	0.7383	2.2	9.8	0.1232	−27.75	+2.0%	1.1735	4.7472	12.6	25.4	0.7871	−154.47	+0.9%
0.6121	1.0807	3.2	13.6	0.1801	−41.65	−2.5%	1.2183	2.6036	0	0	0.4340	−177.25	+0.4%
0.8391	1.3092	4.2	18.3	0.2238	−71.31	−1.4%	1.3407	4.4728	0	0	0.8391	−188.12	+0.9%
0.9487	3.4361	0	0	0.6121	−100.71	+0.1%	1.5605	5.3095	0	0	0.9804	−247.33	−3.0%
0.9804	1.6850	4.8	21.0	0.2701	−105.68	+1.1%	1.9081	6.0721	0	0	1.1735	−346.16	+0.4%
						N,*N*-Dibutylformamide							
0.3129	0.3883	1.5	6.7	0.0696	1.42	−1.3%	1.0537	3.4189	0	0	0.5939	23.89	−0.4%
0.6548	0.7014	3.1	14.0	0.1284	5.57	−0.7%	1.5530	1.7285	0	0	0.3129	32.85	+0.4%
0.5939	2.4737	5.2	13.1	0.3712	8.43	+1.1%	1.3610	4.2875	0	0	0.8246	35.14	+0.1%
0.8775	1.3794	4.1	18.2	0.2310	13.54	−0.1%	1.6155	4.8204	0	0	0.8775	53.75	−1.0%
0.8246	3.2906	7.0	17.7	0.5085	16.00	+1.6%							
						N,*N*-Dimethylacetamide							
0.2931	0.6098	2.6	10.4	0.1031	−18.28	+0.2%	1.3490	2.2757	11.3	43.9	0.4152	−311.15	−0.6%
0.3301	0.6393	2.9	11.7	0.1102	−22.53	+1.9%	1.3682	2.4024	0	0	0.4227	−338.03	+0.3%
0.3178	1.3607	5.6	14.2	0.2011	−25.30	+2.6%	1.4410	5.0535	0	0	0.9227	−372.58	−1.3%
0.4815	2.0333	10.6	21.3	0.3301	−45.64	−2.7%	1.5353	2.7153	0	0	0.4815	−320.92	+0.3%
0.6559	2.4702	7.7	15.0	0.4356	−83.27	+0.8%	1.9078	6.4423	0	0	1.2039	−619.17	−1.3%
0.9227	1.6853	7.9	31.0	0.2976	−156.58	−1.8%	2.1614	7.0367	0	0	1.3490	−768.78	−0.6%
1.2039	1.6836	9.8	39.6	0.3178	−224.31	+0.8%	2.1979	3.6331	0	0	0.6559	−790.96	+0.6%

Table I (Continued)

$m_{A,i}$, mol kg^{-1}	n_A, mmol	$m_{B,i}$, mmol kg^{-1}	n_B, μmol	m_t, mol kg^{-1}	ΔH, mJ	% Δ[a]	$m_{A,i}$, mol kg^{-1}	n_A, mmol	$m_{B,i}$, mmol kg^{-1}	n_B, μmol	m_t, mol kg^{-1}	ΔH, mJ	% Δ[a]
						N,N-Diethylacetamide							
0.3760	0.7425	3.3	13.1	0.1269	−32.47	+0.3%	1.1170	3.9429	23.1	45.5	0.7254	−244.61	−0.1%
0.4801	1.8407	10.4	20.9	0.3180	−51.00	+0.8%	1.2914	4.8976	25.5	51.7	0.8504	−338.39	+0.7%
0.5678	1.0825	4.8	19.4	0.1862	−70.80	−0.5%	1.5574	5.0711	0	0	0.9607	−466.96	−0.4%
0.5563	2.3056	11.7	24.0	0.3760	−71.44	+2.1%	1.8261	5.8236	0	0	1.1170	−605.60	−2.6%
0.6186	2.3080	12.9	26.5	0.4032	−84.31	+1.3%	1.9238	3.1019	0	0	0.5563	−661.01	+0.3%
0.8504	3.4023	17.3	35.6	0.5678	−156.56	−0.2%	2.1256	6.6469	0	0	1.2914	−816.23	+1.3%
0.9607	3.4202	19.6	39.7	0.6186	−188.77	−0.0%							
						N,N-Dipropylacetamide							
0.2533	0.4830	0	0	0.0763	−13.13	−1.7%	1.1480	4.3930	11.8	23.9	0.7546	−227.38	−2.5%
0.2984	1.2784	2.7	6.8	0.1880	−20.88	−1.3%	1.2867	2.1612	0	0	0.3821	−269.33	−1.4%
0.3821	1.6447	4.8	8.8	0.2690	−28.91	+2.3%	1.6093	5.5647	0	0	1.0182	−413.19	−0.5%
0.4532	1.7009	0	0	0.2943	−40.49	+0.2%	1.6093	3.0581	0	0	0.4901	−455.60	−0.4%
0.6007	2.4961	5.6	13.4	0.3833	−80.74	+0.7%	1.9148	2.9850	0	0	0.5394	−534.39	+1.2%
1.0182	1.3060	4.8	21.0	0.2338	−151.70	+2.3%	1.9148	5.8097	0	0	1.1480	−541.63	+1.2%
0.9535	3.2969	0	0	0.6007	−168.80	+2.7%							
						N,N-Dibutylacetamide							
0.4382	1.7812	18.9	18.7	0.3560	−7.55	+4.0%	1.0006	1.3065	7.8	31.1	0.2534	−47.76	−1.0%
0.4104	0.6412	3.4	13.9	0.1148	−9.93	−0.6%	0.9009	3.3959	17.8	35.9	0.5934	−50.46	+1.2%
0.4249	1.7589	8.9	18.2	0.2872	−12.53	+1.1%	0.5449	1.0319	4.6	18.1	0.1788	−60.02	+2.4%
0.5934	2.3740	16.8	24.8	0.4382	−18.74	+3.1%	1.4566	2.2668	0	0	0.4104	−111.77	+0.1%
0.5449	1.0319	4.6	18.1	0.1788	−20.02	+2.4%	1.4964	4.5493	0	0	0.9009	−122.17	+0.9%
0.6380	2.5213	12.9	26.4	0.4249	−27.44	+2.9%	1.6647	4.9680	0	0	1.0006	−143.47	−0.1%
						N,N-Dipentylacetamide							
0.2477	0.5612	0	0	0.0848	8.67	−2.8%	0.7812	2.6385	0	0	0.4883	65.95	+0.7%
0.3021	0.6703	1.5	6.7	0.1013	12.88	+1.0%	0.9982	3.6640	13.2	20.1	0.7094	81.95	−1.1%
0.4043	0.5480	2.0	8.8	0.0967	15.86	+0.6%	0.9093	3.4343	8.9	18.6	0.5879	89.66	−0.0%
0.4883	0.6739	2.3	10.5	0.1165	23.15	−0.3%	1.5544	4.4870	0	0	0.9093	205.45	+0.8%
0.4860	1.9447	0	0	0.3021	32.77	+1.2%	1.7279	2.4289	0	0	0.4489	230.86	+0.6%
0.6445	2.2172	0	0	0.4043	48.26	+3.6%	1.7279	4.8581	0	0	0.9982	235.08	−1.5%

[a] $\Delta\ \% = 100[\Delta H(\text{exptl}) - \Delta H(\text{calcd})]/\Delta H(\text{exptl})$, where ΔH(calcd) is calculated from eq 3.

Table II. Enthalpic Interaction Coefficients of Amides in NMF

compd	B_2^h, J kg mol^{-2}	B_3^h, J kg^2 mol^{-3}
DMF	+66.7 (0.8)[a]	−4.8 (0.3)[a]
DEF	+97 (1)	−6.4 (0.6)
DBF	+15.26 (0.03)	
DMA	+162 (1)	−7.6 (0.5)
DEA	+182 (2)	−10.7 (0.7)
DPrA	+163 (2)	−14 (1)
DBA	+55.5 (0.5)	−4.5 (0.3)
DPeA	−100 (2)	+12 (1)
NBF	−78 (1)	+5.6 (0.5)
NPeF	−125 (2)	+10.7 (0.9)
NMA	−1.12 (0.02)	−0.43 (0.01)
NEA	−31.9 (0.3)	
NPrA	−76.3 (0.9)	+4.5 (0.4)
NBA	−135 (2)	+10.2 (0.9)

[a] The numbers in parentheses are the standard deviations of the coefficients.

for dialkylformamides are more negative than those of isomeric dialkylacetamides, while the B_3^h values are more positive. These differences are more pronounced in NMF. Contrary to the situation in DMF as solvent, no differences are observed between the enthalpic interaction coefficients of isomeric *N*-alkylacetamides and *N*-alkylformamides.

Registry No. NBF, 871-71-6; NPeF, 2591-79-9; NMA, 79-16-3; NEA, 625-50-3; NPrA, 5331-48-6; NBA, 1119-49-9; DMF, 68-12-2; DEF, 617-84-5; DBF, 761-65-9; DMA, 127-19-5; DEA, 685-91-6; DPrA, 1116-24-1; DBA, 1563-90-2; DPeA, 16238-16-7; NMF, 123-39-7.

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Received for review March 17, 1986. Revised October 16, 1986. Accepted January 19, 1987. This work has been carried out under the auspices of the Netherlands Foundation for Chemical Research (SON) and with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).