Mixing Enthalpies of Alkylureas with Electrolytes in Water at 298.15 K

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Excess enthalpies of several alkylureas (methylurea, 1,1-dimethylurea, 1,1-dimethylurea, and tetramethylurea) with some aqueous electrolytes (NaCl, NaBr, Me_4NBr, and Bu_4NBr) have been determined by flow microcalorimetry at 298.15 K. Enthalpic pair interaction coefficients, h_{NE}, of the virial expansion of the mixing enthalpy were derived. These are negative for the interaction of methylurea and 1,1-dimethylurea with NaCl, NaBr, and Me_4NBr. The remaining systems exhibit positive coefficients. A linear dependence between h_{EN} and the number of CH_3 groups in the hydrocarbon chain of alkylurea is observed.

Introduction

This work is a continuation of our studies on thermodynamic properties of nonionic solutes with electrolytes in water.[1−3] These studies form a part of a program with the aim of obtaining information on nonelectrolyte−electrolyte interactions in water. We present here some new experimental data on mixing enthalpies of some alkylureas (methylurea, 1,1-dimethylurea, 1,3-dimethylurea, and tetramethylurea) with NaCl, NaBr, Me_4NBr, and Bu_4NBr. The results have been rationalized by means of enthalpic pair interaction coefficients as derived from the virial expansion of the excess enthalpies. These coefficients are a measure of solute−solute interactions, which include any contribution arising from the change in solvation of both solvated solutes as they approach each other.

Experimental Section

Materials. Methylurea (Aldrich, stated purity 97 mol %) was twice recrystallized from anhydrous ethanol and dried for 48 h in a vacuum desiccator. 1,1-Dimethylurea and 1,3-dimethylurea were purchased from Aldrich (stated purity 99 mol %), and they were used as received after they were dried in a vacuum desiccator for 48 h at 303 K. Tetramethylurea (Aldrich, stated purity 99 mol %) was used as received. NaCl and NaBr (Merck, p.a.) were oven-dried for 2 days at 393 K. Tetramethylammonium bromide (Me_4NBr) and tetrabutylammonium bromide (Bu_4NBr) from Fluka of the best quality available were purified and checked as described by Conway et al.[4] All reagents were kept in a vacuum desiccator with P_2O_5. Solutions were prepared by weight with previously degassed water obtained from a Milli-Q water system (Millipore, $\kappa < 10^{-6}$ S cm^{-1}).

Apparatus and Procedure. Enthalpies of dilution and mixing were determined with a ThermoMetric (TAM 2277) flow microcalorimeter operating at (298.15 ± 0.01) K. Details of this apparatus, associated equipment, and the experimental procedure adopted have been reported in previous papers.[5,6] Solutions were prepared by weight with an uncertainty of ±0.1 mg. The flow rate of each pump was controlled after each dilution or mixing experiment by weighing the liquids pumped. The total flow rate of liquids through the microcalorimeter was ca. 0.51 cm^3 min^{-1}.

Table 1. Enthalpies of Dilution of 1,1-Dimethylurea, 1,3-Dimethylurea, and Tetramethylurea in Water at 298.15 K

m_i / mol kg^{-1}	m_f / mol kg^{-1}	$\Delta_{dil}H_{m,N}$ / J mol^{-1}	m_i / mol kg^{-1}	m_f / mol kg^{-1}	$\Delta_{dil}H_{m,N}$ / J mol^{-1}
		1,1-Dimethylurea			
0.1997	0.0982	0.74	0.7141	0.4781	−8.69
0.2941	0.0923	−0.64	0.8982	0.2733	−23.6
0.2941	0.1414	1.01	0.8982	0.4218	−18.8
0.2941	0.1461	1.48	0.8982	0.5987	−14.8
0.4305	0.1220	1.18	0.9793	0.2529	−36.0
0.4305	0.2068	0.31	0.9793	0.4673	−24.6
0.4977	0.1546	−4.98	0.9793	0.6982	−17.2
0.4977	0.2374	−1.61	1.4958	0.4011	−77.3
0.4977	0.3350	−2.62	1.4958	0.6784	−56.9
0.6015	0.1585	−11.0	2.0082	0.5250	−135.8
0.6015	0.2912	−7.95	2.0082	0.9643	−103.9
0.6015	0.4322	−5.41	2.3180	0.6700	−146.8
0.7041	0.9193	−14.4	2.3180	1.0361	−123.1
0.7141	0.3377	−10.2	2.3180	1.4820	−85.8
		1,3-Dimethylurea			
0.2512	0.1251	−6.5	0.9800	0.4771	−86.7
0.4852	0.2395	−20.1	0.9800	0.6417	−63.7
0.4915	0.0810	−20.5	0.9800	0.8094	−35.1
0.4915	0.2409	−17.6	1.5233	0.2355	−234.4
0.4915	0.2421	−19.3	1.5233	0.4782	−224.1
0.4915	0.3262	−15.0	1.5233	0.7179	−186.9
0.7263	0.1179	−52.7	1.5233	0.7278	−187.4
0.7263	0.2371	−53.0	1.5233	0.9849	−135.6
0.7263	0.3575	−45.9	1.6942	0.5268	−249.5
0.7263	0.4791	−34.9	1.6942	0.8026	−214.2
0.7263	0.6021	−19.3	1.6942	1.3862	−85.9
0.7374	0.3604	−49.6	2.2554	0.6817	−391.9
0.9800	0.1562	−101.8	2.2554	1.4303	−238.2
0.9800	0.3153	−100.2	2.2554	1.8325	−129.3
0.9800	0.4707	−84.8			
		Tetramethylurea			
0.1321	0.0216	−231.3	0.5082	0.0825	−858.7
0.1321	0.0434	−185.3	0.5082	0.1660	−698.7
0.1321	0.0654	−140.4	0.5082	0.2502	−518.3
0.1321	0.0874	−96.5	0.5082	0.3353	−354.1
0.1321	0.1097	−48.1	0.5082	0.4213	−174.8
0.2685	0.1291	−293.3	0.6835	0.1064	−1145.7
0.3231	0.0520	−549.0	0.6835	0.2157	−933.6
0.3231	0.1047	−442.9	0.6835	0.3279	−702.9
0.3231	0.1581	−341.0	0.6835	0.4432	−478.7
0.3231	0.2123	−228.9	0.6835	0.5617	−236.3
0.3231	0.2623	−125.4	0.7363	0.3448	−772.2
0.4991	0.2368	−520.6			

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10.1021/je000326n CCC: $20.00
Published on Web 02/10/2001

Table 2. Coefficients of Equation 5 for the Dilution of Ureas in Water at 298.15 K

	h_{NN}	h_{NNN}	h_{NNNN}	s
	J kg mol^{-2}	J kg^2 mol^{-3}	J kg^3 mol^{-4}	J mol^{-1}
methylurea[a]	−85 (1)	21 (1)		
1,1-dimethylurea	−37 (15)	80 (15)	−15 (4)	3.6
1,3-dimethylurea	−29 (15)	164 (14)	−28 (4)	3.9
tetramethylurea	2086 (32)	−106 (39)		5.2

[a] Barone et al. (1979). Numbers in parentheses are 95% confidence limits.

Electrical calibration was performed after each run. The accuracy of the experimental method was tested by measuring the enthalpies of dilution for freshly prepared urea solutions in the molality range of 0−2.0 mol kg^{-1}. The measured values of the relative apparent molar enthalpy ϕ_L for the urea solutions were in good agreement with those reported in the literature (Marsh, 1987)[7] with an average deviation of less than ±1%.

Results and Discussion

The excess enthalpy $H^E(m_N,m_E)$ of a solution containing 1 kg of water, m_N mol of a nonelectrolyte N, and m_E mol of an electrolyte E can be expressed in terms of a virial expansion of the molalities:[8]

$$H^E(m_N, m_E) = H(m_N, m_E) - H_w^0 - H_N^0 m_N - H_E^0 m_E \quad (1)$$
$$= h_{NN} m_N^2 + 2h_{NE} m_N m_E + h_{EE} m_E^2 + h_{NNN} m_N^3 + 3h_{NNE} m_N^2 m_E + 3h_{NEE} m_N m_E^2 + h_{EEE} m_E^3 \ldots$$

Here, $H(m_N, m_E)$ is the absolute enthalpy of the solution, H_w^0 is the standard enthalpy of 1 kg of water, and H_N^0 and H_E^0 are the limiting partial molar enthalpies of N and E, respectively. The h_{ij} and h_{ijk} terms are enthalpic virial coefficients representing interactions between the sub-

Table 3. Enthalpies of Mixing of Ureas with Electrolytes in Water at 298.15 K

$m_{i,N}$	$m_{i,E}$	$m_{f,N}$	$m_{f,E}$	$\Delta_{mix}H$	ΔH^*	$m_{i,N}$	$m_{i,E}$	$m_{f,N}$	$m_{f,E}$	$\Delta_{mix}H$	ΔH^*
mol kg^{-1}	mol kg^{-1}	mol kg^{-1}	mol kg^{-1}	J kg^1	J kg^{-1}	mol kg^{-1}	mol kg^{-1}	mol kg^{-1}	mol kg^{-1}	J kg^1	J kg^{-1}
Methylurea											
NaCl								Me_4NBr			
0.2581	0.2442	0.1258	0.1252	−4.7	−6.2	0.2514	0.2527	0.1256	0.1265	41.8	−10.2
0.2581	0.4935	0.1261	0.2524	18.5	−11.3	0.2514	0.4994	0.1273	0.2465	150.3	−12.9
0.2581	0.7430	0.1264	0.3791	71.6	−15.5	0.2514	0.7579	0.1290	0.3689	302.2	−15.0
0.5035	0.2442	0.2436	0.1261	−7.6	−12.2	0.5018	0.2527	0.2488	0.1274	33.6	−21.4
0.5035	0.4935	0.2441	0.2542	10.4	−22.5	0.5018	0.4994	0.2522	0.2484	132.7	−33.5
0.5035	0.7430	0.2447	0.3819	59.5	−30.8	0.5018	0.7579	0.2556	0.3718	277.9	−42.1
0.7474	0.2442	0.3590	0.1269	−9.7	−18.6	0.7596	0.2527	0.3736	0.1284	26.4	−33.1
0.7474	0.4935	0.3599	0.2559	3.2	−34.1	0.7596	0.4994	0.3788	0.2504	116.0	−54.5
0.7474	0.7430	0.3607	0.3844	47.8	−46.7	0.7596	0.7579	0.3841	0.3747	250.9	−73.2
NaBr								Bu_4NBr			
0.2514	0.2616	0.1241	0.1325	−3.6	−9.5	0.2514	0.0598	0.1238	0.0303	8.3	11.0
0.2514	0.4984	0.1245	0.2517	23.5	−15.2	0.2514	0.1193	0.1249	0.0600	2.2	21.8
0.2514	0.7623	0.1249	0.3837	87.4	−19.2	0.2514	0.2653	0.1275	0.1307	−88.3	44.1
0.2581	0.2616	0.1288	0.1310	−3.9	−9.9	0.5018	0.0598	0.2453	0.0306	22.6	22.2
0.2581	0.4984	0.1292	0.2489	22.8	−15.9	0.5018	0.1193	0.2474	0.0605	26.6	43.1
0.5035	0.2616	0.2494	0.1320	−9.9	−19.0	0.5018	0.2653	0.2526	0.1318	−43.2	86.1
0.5035	0.4984	0.2502	0.2508	9.8	−32.0	0.7596	0.0598	0.3684	0.0308	37.8	32.9
0.7474	0.2616	0.3670	0.1331	−15.1	−28.5	0.7596	0.1193	0.3717	0.0609	52.5	64.5
0.7474	0.4984	0.3681	0.2529	−2.1	−48.3	0.7596	0.2653	0.3795	0.1328	9.1	134.1
0.7596	0.2616	0.3691	0.1345	−15.3	−28.9						
0.7596	0.4984	0.3703	0.2555	−2.4	−48.9						
0.7596	0.7623	0.3715	0.3895	47.34	−67.1						
1,1-Dimethylurea											
NaCl								Me_4NBr			
0.1997	0.2095	0.0994	0.1052	−1.7	−0.4	0.1972	0.1997	0.0941	0.1044	31.3	−1.7
0.1997	0.5965	0.0998	0.2984	46.2	−2.5	0.2030	0.1985	0.1039	0.0969	29.9	−2.9
0.1997	0.9983	0.1002	0.4976	162.3	−6.8	0.2030	0.5765	0.1060	0.2755	209.4	4.4
0.6015	0.2095	0.2950	0.1068	−5.9	−2.3	0.2030	0.7754	0.1070	0.3665	327.2	−1.3
0.6015	0.5965	0.2960	0.3029	37.0	−9.4	0.4305	0.1997	0.2036	0.1052	25.8	−6.6
0.6015	0.9983	0.2972	0.5051	149.8	−17.1	0.4305	0.6099	0.2085	0.3146	217.1	−4.1
0.9793	0.2095	0.4682	0.1093	−17.3	−3.1	0.5984	0.1997	0.2812	0.1059	20.1	−10.5
0.9793	0.5965	0.4700	0.3102	20.6	−15.5	0.5984	0.6099	0.2879	0.3165	205.5	−13.6
0.9793	0.9983	0.4718	0.5173	130.1	−26.3	0.6052	0.1985	0.3051	0.0984	19.5	−10.8
NaBr						0.6052	0.5765	0.3115	0.2798	182.2	−19.9
0.1972	0.2016	0.0928	0.1067	−2.0	−3.1	1.0057	0.1997	0.4624	0.1079	0.9	−18.0
0.1972	0.6028	0.0933	0.3176	−55.7	−5.3	1.0057	0.6099	0.4737	0.3226	168.3	−37.9
0.1972	0.9990	0.0938	0.5238	−188.8	−4.6	1.0061	0.1985	0.4874	0.1023	0.8	−17.6
0.4305	0.2009	0.2105	0.1027	−6.9	−7.3	1.0061	0.5765	0.4979	0.2912	147.2	−41.9
0.4305	0.5982	0.2116	0.3042	40.4	−18.7	1.0061	0.7754	0.5031	0.3876	265.9	−46.0
0.4305	1.0014	0.2127	0.5067	165.3	−28.4			Bu_4NBr			
0.5984	0.2016	0.2772	0.1082	−11.5	−10.3	0.2030	0.0591	0.1044	0.0287	10.2	13.9
0.5984	0.6028	0.2787	0.3221	32.8	−25.9	0.2030	0.1146	0.1052	0.0552	7.6	26.2
0.5984	0.9990	0.2802	0.5313	154.9	−36.1	0.2030	0.1776	0.1062	0.0847	−12.3	40.9
1.0057	0.2009	0.4812	0.1048	−30.7	−17.5	0.6052	0.0591	0.3068	0.0291	34.1	40.4
1.0057	0.5982	0.4837	0.3105	−3.2	−48.7	0.6052	0.1146	0.3092	0.0560	56.4	77.6
1.0057	1.0014	0.4862	0.5172	105.2	−74.9	0.6052	0.1776	0.3119	0.0861	62.4	118.3
						1.0061	0.0591	0.5048	0.0294	48.5	66.7
						1.0061	0.1146	0.5089	0.0566	95.1	128.4
						1.0061	0.1776	0.5134	0.0870	127.9	196.1

Table 3 (Continued)

$m_{i,N}$ / mol kg^{-1}	$m_{i,E}$ / mol kg^{-1}	$m_{f,N}$ / mol kg^{-1}	$m_{f,E}$ / mol kg^{-1}	$\Delta_{mix}H$ / J kg^{1}	ΔH^* / J kg^{-1}	$m_{i,N}$ / mol kg^{-1}	$m_{i,E}$ / mol kg^{-1}	$m_{f,N}$ / mol kg^{-1}	$m_{f,E}$ / mol kg^{-1}	$\Delta_{mix}H$ / J kg^{1}	ΔH^* / J kg^{-1}
					1,3-Dimethylurea						
		NaCl						Me_4NBr			
0.2512	0.2599	0.1254	0.1309	4.5	4.0	0.2512	0.2511	0.1341	0.1170	50.4	0.8
0.2512	0.4914	0.1257	0.2456	36.7	9.3	0.2512	0.5005	0.1359	0.2298	167.9	5.3
0.2512	0.7507	0.1260	0.3743	101.9	14.8	0.2512	0.7228	0.1373	0.3276	305.5	11.8
0.4852	0.2599	0.2400	0.1313	3.4	7.0	0.4852	0.2511	0.2569	0.1181	46.5	1.0
0.4852	0.4914	0.2405	0.2478	39.7	16.3	0.4852	0.5005	0.2602	0.2321	165.9	7.5
0.4852	0.7507	0.2411	0.3777	110.4	27.3	0.4852	0.7228	0.2631	0.3308	305.7	16.3
0.7374	0.2599	0.3613	0.1326	−6.7	9.2	0.7374	0.2511	0.3870	0.1193	32.8	−0.0
0.7374	0.4914	0.3620	0.2501	33.1	22.0	0.7374	0.5005	0.3920	0.2344	153.9	8.1
0.7374	0.7507	0.3629	0.3812	108.8	37.9	0.7374	0.7228	0.3964	0.3343	296.7	20.1
		NaBr						Bu_4NBr			
0.2488	0.2492	0.1233	0.1257	5.7	2.4	0.4871	0.0588	0.2419	0.0296	24.4	32.9
0.2488	0.4964	0.1237	0.2496	52.0	15.3	0.4871	0.1146	0.2439	0.0572	39.8	63.3
0.2488	0.7408	0.1241	0.3714	124.1	26.0	0.7532	0.0588	0.3703	0.0299	27.6	49.5
0.2488	0.2492	0.1230	0.1260	7.3	4.0	0.7532	0.1146	0.3733	0.0578	59.3	96.3
0.2488	0.4964	0.1234	0.2502	49.6	12.9	0.7532	0.1720	0.3764	0.0860	75.4	143.4
0.2488	0.7408	0.1238	0.3723	122.8	24.6	0.9782	0.0588	0.4768	0.0301	21.0	63.9
0.4871	0.2492	0.2392	0.1268	1.2	2.1	0.9782	0.1146	0.4808	0.0583	64.8	122.9
0.4871	0.4964	0.2400	0.2519	43.9	11.4	0.9782	0.1720	0.4848	0.0868	94.1	183.4
0.4871	0.7408	0.2407	0.3747	129.2	35.1	1.4393	0.0588	0.6897	0.0306	−24.9	93.4
0.7532	0.2492	0.3661	0.1281	−12.9	1.3	1.4393	0.1146	0.6956	0.0592	46.5	180.3
0.7532	0.4964	0.3673	0.2544	31.7	12.5	1.4393	0.1720	0.7014	0.0882	103.0	268.1
0.9782	0.2492	0.4739	0.1285	−34.4	0.7						
1.4393	0.2492	0.6853	0.1305	−112.4	−2.3						
1.4393	0.7408	0.6898	0.3858	25.6	40.9						
					Tetramethylurea						
		NaCl						Me_4NBr			
0.1321	0.5003	0.0680	0.2428	32.2	12.2	0.2858	0.2511	0.1519	0.1176	18.1	9.5
0.1321	1.0024	0.0683	0.4842	182.6	22.3	0.2858	0.5005	0.1539	0.2311	145.8	24.1
0.3231	0.5003	0.1645	0.2455	4.9	28.9	0.2858	0.7228	0.1556	0.3294	291.8	39.0
0.3231	1.0024	0.1653	0.4896	173.5	57.0	0.5222	0.2511	0.2742	0.1193	−69.4	16.5
0.5082	0.5003	0.2496	0.2546	−55.8	44.0	0.5222	0.5005	0.2778	0.2343	67.0	39.8
0.5082	1.0024	0.2508	0.5077	133.3	92.4	0.5222	0.7228	0.2809	0.3340	221.7	63.3
0.6835	0.5003	0.3415	0.2504	−136.6	64.9	0.7068	0.2511	0.3677	0.1205	−171.5	24.2
0.6835	1.0024	0.3431	0.4993	71.9	132.8	0.7068	0.5005	0.3725	0.2367	−27.9	54.6
1.0226	0.5003	0.4885	0.2613	−369.0	103.5	0.7068	0.7228	0.3367	0.3375	133.8	84.9
1.0226	0.5003	0.5019	0.2547	−365.4	107.9			Bu_4NBr			
1.0226	1.0024	0.4909	0.5212	−117.3	214.7	0.2685	0.0600	0.1292	0.0311	−0.8	40.0
1.0226	1.0024	0.5043	0.5080	−111.5	221.1	0.2685	0.1148	0.1303	0.0591	20.9	76.7
		NaBr				0.3150	0.0600	0.1512	0.0312	−9.6	44.8
0.2685	0.2664	0.1256	0.1418	−29.9	1.4	0.3150	0.1148	0.1525	0.0592	17.0	86.5
0.2685	0.4759	0.1259	0.2527	7.4	10.5	0.3150	0.1763	0.1538	0.0902	29.6	133.1
0.2685	0.7357	0.1263	0.3895	85.6	24.9	0.4946	0.0600	0.2371	0.0312	−54.0	72.6
0.3150	0.1911	0.1518	0.0990	−48.8	1.3	0.4946	0.1148	0.2391	0.0593	−2.1	139.6
0.3150	0.4759	0.1511	0.2476	−3.9	13.1	0.4946	0.1763	0.2413	0.0903	37.3	213.0
0.3150	0.7357	0.1516	0.3816	72.7	25.8	0.7904	0.0600	0.3728	0.0317	−188.3	121.2
0.3181	0.2420	0.1566	0.1229	−44.8	3.4	0.7904	0.1148	0.3759	0.0602	−98.4	226.4
0.3181	0.4753	0.1571	0.2406	−6.0	12.4	0.7904	0.1763	0.3794	0.0917	−17.6	341.4
0.3181	0.7659	0.1576	0.3864	80.3	25.3						
0.4946	0.1911	0.2359	0.1000	−118.0	4.2						
0.4991	0.1911	0.2380	0.1000	−120.7	3.6						
0.4991	0.4759	0.2309	0.2557	−74.3	16.4						
0.4991	0.7357	0.2317	0.3941	12.4	39.4						
0.5252	0.2420	0.2556	0.1242	−127.4	7.3						
0.5252	0.4753	0.2564	0.2433	−82.6	22.2						
0.5252	0.7659	0.2573	0.3907	12.1	43.5						
0.7363	0.2664	0.3460	0.1412	−246.7	14.1						
0.7363	0.4759	0.3469	0.2517	−196.2	36.5						
0.7363	0.7357	0.3481	0.3879	−102.3	66.6						
0.7904	0.2664	0.3681	0.1423	−278.2	21.6						
0.7904	0.4759	0.3691	0.2536	−226.1	45.5						
0.7904	0.7357	0.3704	0.3909	−130.9	77.0						
0.8447	0.2420	0.4040	0.1263	−322.2	22.3						
0.8447	0.4753	0.4052	0.2473	−265.2	49.4						
0.8447	0.7659	0.4067	0.3971	−154.9	86.3						

scripted species. To evaluate these coefficients, the excess enthalpies of the binary solutions must be known. Introducing an auxiliary function ΔH^*, defined as

$$\Delta H^* = \Delta_{mix}H_{N,E} - \Delta_{dil}H_N - \Delta_{dil}H_E = H^E(m_N,m_E) - H^E(m_N) - H^E(m_E) \quad (2)$$

and combining eqs 1 and 2 yields

$$\Delta H^* = 2h_{NE}m_Nm_E + 3h_{NNE}m_N{}^2m_E + 3h_{NEE}m_Nm_E{}^2 + \ldots \quad (3)$$

which can be expressed in a general form as

$$\Delta H^* = A_0m_Nm_E + A_1m_N{}^2m_E + A_2m_Nm_E{}^2 + \ldots \quad (4)$$

where $A_0 = 2h_{NE}$, $A_1 = 3h_{NNE}$, and $A_3 = 3h_{NEE}$. To obtain

Table 4. Coefficients for Equation 4 and Standard Deviation of the Fit[a]

	A_0	A_1	A_2	s
	J kg mol^{-2}	J kg^2 mol^{-3}	J kg^2 mol^{-3}	J kg^{-1}
		Methylurea		
NaCl				
NaCl	−416 (3)	−68 (8)	272 (7)	0.04
NaBr	−631 (30)	−108 (75)	594 (92)	1.2
Me_4NBr	−645 (125)	−560 (333)	1021 (343)	2.5
Bu_4NBr	3053 (97)	−70 (300)	−3008 (721)	1.0
		1,1-Dimethylurea		
NaCl	−42 (36)	−9 (82)	−152 (77)	2.1
NaBr	−283 (76)	−293 (190)	271 (159)	3.1
Me_4NBr	−224 (132)	−612 (296)	849 (404)	3.4
Bu_4NBr	4672 (92)	−279 (171)	−1669 (1219)	0.6
		1,3-Dimethylurea		
NaCl	239 (32)	−222 (88)	312 (85)	0.6
NaBr	260 (130)	−1143 (361)	1062 (355)	2.5
Me_4NBr	20 (46)	−333 (118)	820 (141)	1.0
Bu_4NBr	4670 (90)	−324 (143)	−1444 (1016)	0.8
		Tetramethylurea		
NaCl	668 (82)	341 (155)	−36 (181)	2.7
NaBr	−44 (87)	668 (248)	920 (221)	4.0
Me_4NBr	499 (106)	−244 (289)	821 (295)	1.9
Bu_4NBr	9706 (459)	1315 (1329)	−3236 (5454)	1.8

[a] Numbers in parentheses are 95% confidence limits.

Table 5. Enthalpic Pair Interaction Coefficients, h_{NE}/(J kg mol^{-2}), for Ureas with Electrolytes in Water at 298.15 K[a]

	NaCl	NaBr	Me_4NBr	Bu_4NBr
urea	−537 (4)	−675 (2)	−756 (19)	804 (40)
methylurea	−208 (3)	−316 (15)	−323 (63)	1527 (49)
1,1-dimethylurea	−21 (18)	−142 (38)	−112 (66)	2336 (46)
1,3-dimethylurea	119 (16)	130 (65)	10 (23)	2335 (45)
tetramethylurea	328 (19)	−22 (44)	250 (53)	4853 (230)

[a] Numbers in parentheses are 95% confidence limits

the experimental quantity ΔH^*, it is necessary to know the dilution enthalpies of binary mixtures. For NaCl,[9] NaBr,[9] Me_4NBr,[10] and methylurea,[11] values of dilution enthalpies were taken from the literature. In the cases of 1,1-dimethylurea and 1,3-dimethylurea, the corresponding data of enthalpies of dilution found in the literature did not yield coherent results when they were integrated in eq 2. Thus, dilution experiments with those alkylureas and tetramethylurea were performed. The experimental results are given in Table 1.

The molar enthalpy of dilution of a nonelectrolyte from an initial molality m_i to a final molality m_f, $\Delta_{dil}H_m(m_i \rightarrow m_f)$, can be expressed as[12]

$$\Delta_{dil}H_m(m_i \rightarrow m_f) = h_{NN}(m_f - m_i) + h_{NNN}(m_f^2 - m_i^2) + \quad \text{.... (5)}$$

where h_{NN}, h_{NNN}, and so forth are the enthalpic coefficients representing pairwise, triplet, and higher-order interactions between like solvated solute species. Table 2 shows the coefficients of eq 5 which were obtained from least-squares analyses of the results. Table 3 reports the experimentally derived mixing enthalpies corresponding to alkylurea−electrolyte interactions, and in Table 4 the results of fitting these to eq 4 by an analysis of nonlinear least-squares regression are given.

Table 5 collects the enthalpic cross pair interaction coefficients, h_{NE}, for the interaction between alkylureas and the electrolytes studied. We have also included in that table coefficients h_{NE} for the urea−electrolyte interaction. We have calculated those coefficients from the solution enthalpy of Me_4NBr and Bu_4NBr in aqueous urea mixtures[13] and urea in aqueous NaCl and NaBr solutions.[14] Coefficients h_{NNE} and h_{NEE} representing triplet interactions between the subscripted species will not be considered here, because they are complicated quantities encapsulating in one term a great number of interactions that make their interpretation complicated.

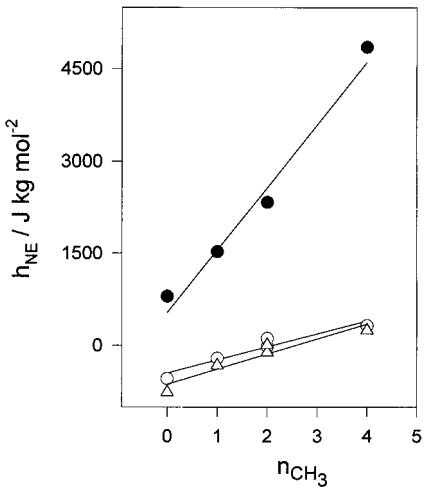

Figure 1. Correlation between enthalpic pair interaction coefficients, h_{EN}, and the number of CH_3 groups in the urea molecule: ●, Bu_4NBr; △, Me_4NBr; ○, NaCl at 298.15 K.

Enthalpic pair interaction coefficents h_{NE} for alkylurea−electrolyte interaction (Table 5) largely depend on the type of urea and electrolyte used. They become more positive in going from urea to tetramethylurea, excepting that for tetramethylurea−NaBr interaction. It is interesting to note the change in the sign of h_{NE} relative to the interaction of 1,1-dimethylurea and 1,3-dimethylurea with NaCl, NaBr, and Me_4NBr. Whereas for the former alkylurea h_{NE} is negative, for the latter it is positive. Nevertheless, identical enthalpic pair interaction coefficients for the interaction of the above isomeric ureas with Bu_4NBr are obtained. On the other hand, with this last electrolyte all coefficients h_{NE} are positive and they increase linearly with the number of methyl groups in the urea molecule, as is shown in Figure 1. A similar pattern is also observed for NaCl and Me_4NBr in their interactions with ureas. Nevertheless, in the case of the interaction of NaBr with ureas that linear dependence is not found.

$$h_{EN}(\text{NaCl + ureas}) = -447.2 + 212.9n_{CH_3} \qquad r^2 = 0.92$$

$$h_{EN}(\text{Me}_4\text{NBr + ureas}) = -625.7 + 244.2n_{CH_3} \qquad r^2 = 0.98$$

$$h_{EN}(\text{Bu}_4\text{NBr + ureas}) = -541.9 + 1016.1n_{CH_3} \qquad r^2 = 0.91$$

The slope values of the above plots represent the overall contribution of the group CH_3 to the coefficient h_{EN}. In all cases this is positive, which means that such interactions contribute in a repulsive sense to the corresponding free energy pair interaction coefficient.

Enthalpic pair interaction coefficients represent the thermochemical result when two solvated solutes interact in solution. The positive values of the coefficients h_{NE} showed in Table 5 could be ascribed to the predominance of partial desolvation of solutes (endothermic effect, positive

contribution to h_{NE}) against solute−solute interactions, which contribute negatively to the value of h_{NE}.

Literature Cited

(1) Muñoz de Miguel, E.; Yanes, C.; Maestre, A. Enthalpy of Interaction of Several Electrolytes with 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidone in Water at 298.15 K. *Thermochim. Acta* **1999**, *331*, 27−36.

(2) García-Pañeda, E.; Maestre, A.; Yanes, C.; Maestre, A. Activity Coefficients for NaCl in (w)Dimethylformamide + (1-w)Water Mixtures at 25 °C. *J. Chem. Eng. Data* **1999**, *44*, 1055−1057.

(3) Muñoz de Miguel, E.; Yanes, C.; García-Pañeda; Mozo-Llamazares, E.; Maestre, A. Enthalpy of Interaction of Some Electrolytes with Dimethyl Sulfoxide in Water at 298.15 K. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2533−2536.

(4) Conway, B. E.; Verrall, R. E.; Desnoyers, J. E. Partial Molal Volumes of Tetraalkylammmonium Halides and Assignment of Individual Ionic Contributions. *Trans. Faraday Soc.* **1966**, *62*, 2738−2749.

(5) Yanes, C.; Sánchez-Montalvo, R.; Calvente, J. J.; Maestre, A. Enthalpy of Dilution of Some Electrolytes in Water at 298.15 K. *Thermochim. Acta* **1994**, *236*, 105−112.

(6) Sánchez-Montalvo, R.; Calvente, J. J.; Yanes, C.; Maestre, A. Enthalpy of Interaction of Some Electrolytes with 2-Methyl-2-butanol in Water at 25 °C. *J. Solution Chem.* **1995**, *24*, 953−965.

(7) Head, A. J.; Sabbah, R. *Recommended Reference Materials for the Realization of Physicochemical Properties*; Blackwell: Oxford, 1987; Chapter 7.

(8) Franks, F.; Pedley, M. Solute Interactions in Dilute Aqueous Solutions. *J. Chem. Soc., Faraday Trans.* **1981**, *77*, 1341−1349.

(9) Fortier, J.-L.; Desnoyers, J. E. Thermodynamic Properties of Alkali Halides. V. Temperature and Pressure Dependence of Excess Free Energies in Water. *J. Solution Chem.* **1976**, *5*, 297−308.

(10) Fortier, J.-L.; Leduc, P.-A.; Picker, P.; Desnoyers, J. E. Enthalpies of Dilution of Electrolytes by Flow Microcalorimetry. *J. Solution Chem.* **1973**, *2*, 467−475.

(11) Barone, G.; Castronuovo, G.; Elia, V.; Menna, A. Heat of Dilution of Monomethylurea in Aqueous Solutions at 25 °C. *J. Solution Chem.* **1979**, *8*, 157−163.

(12) Desnoyers, J. E.; Perron, G.; Avédikian, L.; Morel, J.-P. Enthalpies of the Urea-tert-Butanol-Water System at 25 °C. *J. Solution Chem.* **1976**, *5*, 631−644.

(13) Cassel, R. B.; Wen, W.-Y. Thermodynamics of Transfer of Three Tetraalkylammonium Bromides from Water to Aqueous Urea Solutions at 25 °C. *J. Phys. Chem.* **1972**, *76*, 1369−1375.

(14) Schrier, M. Y.; Turner, P. J.; Schrier, E. E. Thermodynamic Quantities for the Transfer of Urea from Water to Aqueous Electrolyte Solutions. *J. Phys. Chem.* **1975**, *79*, 1391−1396.

Received for review October 2, 2000. Accepted December 7, 2000.

JE000326N