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Note

HEAT OF DILUTION OF AQUEOUS MIXTURES OF *N*-ALKYLATED AMIDES AT 313.15 K

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Experimental values of heats of dilution in a series of aqueous solutions of *N*-alkylated amides at 313.15 K for methylacetamide (**1**), ethylacetamide (**2**), methylpropionamide (**3**), propylacetamide (**4**), *i*-propylacetamide (**5**), *t*-butylacetamide (**6**), methylisobutyramide (**7**) and butylacetamide (**8**), and a 298.15 K for methylacetamide (**9**) and butylacetamide (**10**), are given. The range of concentration used was: $m = 2.582–0.028$ mol kg^{-1}. The experimental values were correlated using the simple additivity principle of Savage and Wood.

INTRODUCTION

In a previous paper [1] the results of a calculation of thermodynamic excess functions H^E, G^E, S^E on the basis of experimental values of heats of dilution of diluted aqueous solutions of alkylated pyrimidines, aminopurines and caffeine, were presented. The main interest is a search for the dependences describing the solute–solvent interactions of diluted aqueous solutions, to describe the thermodynamic properties of groups of compounds which differ by alkyl-chain length and their position in the molecule [2–5]. This also requires the determination of heats of dilution for chosen *N*-alkylated amides. The values of heats of dilution were used for calculations of the pairwise enthalpy of interaction. A simple additivity principle is used to correlate the experimental data. Beside this group of compounds, investigations of vapor–liquid equilibria and calculations of excess thermodynamic functions at 313.15 K [6] were carried out in this laboratory. The results of heats of dilution are complementary to data for amides at 298.15 K given in the literature by Savage and Wood [7] (*N*-methylacetamide, *N*-methylpropionamide, *N*-butylacetamide, *N*-methylformamide); Wood and Hiltzik [8] (formamide, acetamide, propionamide, *N*,*N*-dimethylformamide); Kresheck [9] (acetamide, *N*,*N*-dimethylformamide).

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TABLE 1

Enthalpies of dilution

m (mol kg^{-1})	$-\Delta H/n_A$ (J mol^{-1})	Δ^a (J mol^{-1})	m (mol kg^{-1})	$-\Delta H/n_A$ (J mol^{-1})	Δ^a (J mol^{-1})
N-*methylacetamide* (313.15 K)					
2.1716	208.6	0.0	0.5655	38.4	−0.2
1.5163	132.1	−0.3	0.4091	24.6	−1.7
1.0771	82.7	0.0	0.2969	17.8	0.2
0.7826	58.1	1.1	0.2187	14.1	0.9
			0.1584		
N-*ethylacetamide* (313.15 K)					
2.1170	432.1	0.0	0.3738	48.6	−1.0
1.4657	272.5	0.0	0.2697	32.5	0.2
1.0346	174.8	0.0	0.1943	21.0	1.1
0.7340	112.0	−0.2	0.1408	16.9	−1.1
0.5240	72.9	0.8	0.1015		
N-*methylpropionamide* (313.15 K)					
1.8685	399.4	−0.5	0.2532	39.2	−2.3
1.3132	267.9	2.0	0.1847	32.8	2.8
0.9334	178.7	−1.4	0.1346	24.9	4.1
0.6664	117.9	0.3	0.0993	23.6	8.0
0.4859	84.2	−2.6	0.0726		
0.3486	57.0	−1.8			
N-*propylacetamide* (313.15 K)					
1.1450	387.2	−0.9	0.2176	46.3	−1.6
0.8146	247.2	1.1	0.1594	34.6	−0.1
0.5801	159.1	3.1	0.1160	26.1	0.9
0.4179	103.2	−1.3	0.0840		
0.3018	69.2	−2.8			
N-i-*propylacetamide* (313.15 K)					
1.8348	636.9	0.0	0.3386	81.5	−2.0
1.2844	434.5	−0.2	0.2457	55.3	−3.3
0.9020	266.6	0.6	0.1776	41.2	0.7
0.6544	182.3	0.3	0.1289	35.7	6.6
0.4739			0.0931		
N-t-*butylacetamide* (313.15 K)					
0.5270	219.3	0.0	0.1483	46.7	1.2
0.3869	145.8	0.1	0.1075	30.4	−1.3
0.2811	97.9	−0.5	0.0781	23.0	0.0
0.2025	63.6	0.3	0.0562		
N-*methylisobutyramide* (313.15 K)					
1.6298	586.8	−0.3	0.3157	98.5	1.9
1.1590	436.0	1.8	0.2308	66.6	−0.8
0.8210	279.6	−2.4	0.1699	50.7	0.6
0.5971	196.5	−0.7	0.1237		
0.4352	141.0	0.5			
N-*butylacetamide* (313.15 K)					
1.6170	1062.8	0.3	0.2107	90.1	−0.3
1.1120	750.1	1.3	0.1530	60.7	−0.8
0.7819	471.5	0.4	0.1114	43.9	1.5

TABLE 1 (continued)

m (mol kg^{-1})	$-\Delta H/n_A$ (J mol^{-1})	Δ[a] (J mol^{-1})	m (mol kg^{-1})	$-\Delta H/n_A$ (J mol^{-1})	Δ[a] (J mol^{-1})
0.5644	315.1	−4.2	0.0813	27.6	−0.3
0.4046	206.1	1.1	0.0607	27.4	5.5
0.2926	139.4	1.4	0.0440		
N-*methylacetamide* (298.15 K)					
2.5823	303.2	−0.2	0.4772	41.7	−0.5
1.8207	206.8	0.8	0.3453	28.3	−1.0
1.2834	133.4	−0.2	0.2511	22.8	1.8
0.9161	87.2	−0.7	0.1824	18.4	3.5
0.6623	60.6	−0.8	0.1328		
N-*butylacetamide* (298.15)					
0.7343	628.5	−0.1	0.1392	80.1	0.6
0.4746	353.1	0.9	0.0933	51.5	0.3
			0.0625		
0.3128	208.9	−1.1	0.0420	34.3	4.4
0.2067	123.0	−0.9	0.0281	18.7	3.2

[a] $\Delta \equiv \Delta H/n_A(\text{expt}) - \Delta H/n_A(\text{calc})$.

EXPERIMENTAL

The substances were produced by 'Chemipan' (Warsaw). The purity of substances was determined chromatographically, and the water contents by the Karl–Fischer method; the values of these determinations corresponded, respectively, to (%): 99.9, 0.11 (**1**); 99.99, 0.01 (**2**); 99.85, 0.11 (**3**); 99.6, 0.0028 (**4**); 99.95, 0.006 (**5**); 99.8, 0.056 (**6**); 99.98, 0.02 (**7**); 99.9, 0.003 (**8**).

The calorimeter used in the determination of heats of dilution was an LKB batch microcalorimeter (Model 10700-2). The microcalorimeter was tested by the determination of the heat of dilution of sucrose and by the Joule's effect generated after each calorimetric measurement. The technique used to measure enthalpies of dilution was as follows: a solution of concentration m_{A_3} was placed in a 4-cm^3 chamber of the calorimetric vessel. Distilled water was placed in a 2-cm^3 chamber. After the measurement of the heat of dilution, a solution of concentration m_F was removed from the calorimeter, and kept for the next experiment. The values of $\Delta H/n_A$ were calculated from the following equation

$$\Delta H/n_A = \sum_{j=1}^{\infty} B_j\left[n_A m_F^j - n_A m_A^j\right]/n_A \qquad (1)$$

where ΔH is the enthalpy change on mixing; n_A represents the number of moles of solute. The coefficients B_j were determined by the least-squares method. The relation between the enthalpy of dilution and the concentration, $H^{ex}(m)$, similar to the literature [7,8] is presented by eqn. (2)

$$H^{ex}(m) = B_1 m + B_2 m^2 + B_3 m^3 + \ldots \qquad (2)$$

TABLE 2

The B_j coefficients (eqn. 1)

No.	Solute	B_1 (J kg mol^{-2})	B_2 (J kg^2 mol^{-3})	B_3 (J kg^3 mol^{-4})	RMSD [a]
		$T = 313.15$ K			
1	CH_3-NH-CO-CH_3	197.3	57.42	−8.81	1.6
2	C_2H_5-NH-CO-CH_3	362.1	163.04	−29.05	4.3
3	CH_3-NH-CO-C_2H_5	570.2	82.35	−14.80	9.8
4	C_3H_7-NH-CO-CH_3	740.5	221.57		4.9
5	$(CH_3)_2$CH-NH-CO-CH_3	748.6	286.70	−65.88	6.2
6	$(CH_3)_3$C-NH-CO-CH_3	985.9	453.22	261.94	1.5
7	CH_3-NH-CO-CH$(CH_3)_2$	1009.7	270.43	−87.73	4.1
8	C_4H_9-NH-CO-CH_3	1211.1	1079.03	−362.97	6.0
		$T = 298.15$ K			
9	CH_3-NH-CO-CH_3	285.7 [b]	45.46	−5.96	3.9
10	C_4H_9-NH-CO-CH_3	1505.8 [c]	1030.07	−296.94	4.9

[a] $\mathrm{RMSD}\ (\mathrm{J\ mol^{-1}}) = \sum_{i=1}^{N}\left[\frac{\left(\Delta H_{(\mathrm{expt.})} - \Delta H_{(\mathrm{calc})}\right)^2}{N-S}\right]^{1/2}$ where N is the number of dilution experiments, S is the number of adjustable parameters.

[b] 235.5 ± 5.4, Savage and Wood [7].

[c] 1477.3 ± 11.7, Savage and Wood [7].

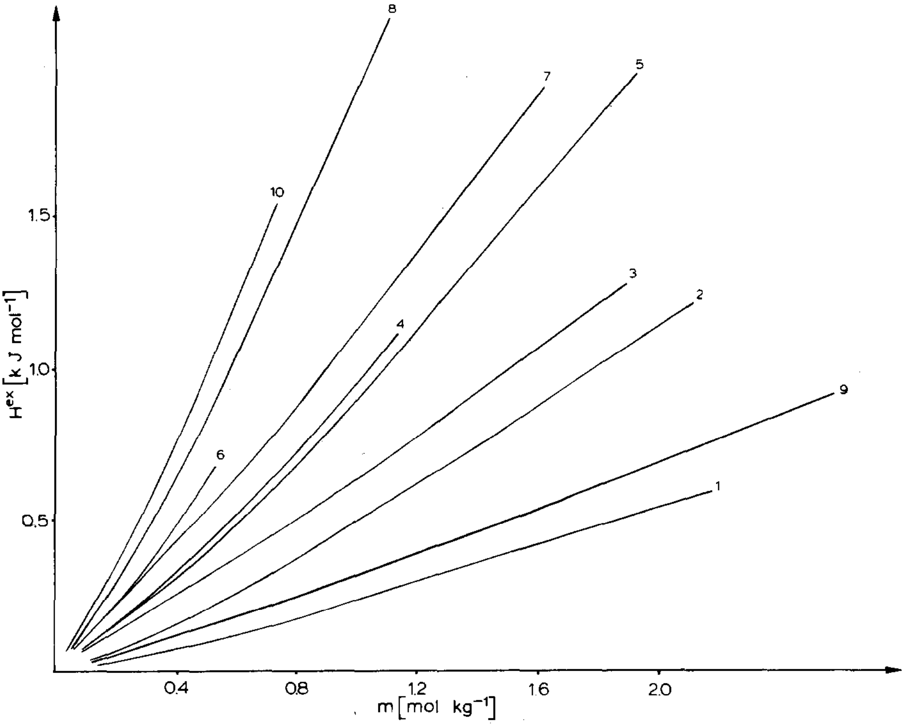

Fig. 1. Enthalpies of dilution vs. concentration of diluted aqueous solutions at 313.15 K for: (**1**) *N*-methylacetamide; (**2**) *N*-ethylacetamide; (**3**) *N*-methylpropionamide; (**4**) *N*-propylacetamide; (**5**) *N*-*i*-propylacetamide; (**6**) *N*-*t*-butylacetamide; (**7**) *N*-methylisobutyramide; (**8**) *N*-butylacetamide; and at 298.15 K for: (**9**) *N*-methylacetamide; (**10**) *N*-butylacetamide.

RESULTS AND DISCUSSION

The raw experimental data are given in Table 1 and the B_j coefficients in eqn. (1) are given in Table 2. Differences, Δ, between experimental and calculated values, $\Delta H/n_A$, from eqn. (1) are given in the third and sixth columns of Table 1. Figure 1 presents graphically the dependence of H^{ex} on the concentration, *m*, calculated by eqn. (2); Fig. 2 shows the dependence of coefficient B_1 on the number of CH_2 groups in the series of *N*-alkylated amides examined.

The results obtained indicate that B_1 increases with the number of alkyl groups, and, for the compounds studied, decreases with increasing temperature. For the temperatures 298.15 and 313.15 K, the corresponding values of B_1 are, respectively CH_3–NH–CO–CH_3, $B_1 = 285.7$ and 197.3; CH_3–NH–CO–C_2H_5, $B_1 = 636.0$ [7] and 570.2; C_4H_9–NH–CO–CH_3, $B_1 =$ 1505.8 and 1211.1 (Table 2). It has been noted that relevant differences in the value of B_1 due to the place of substitution of the alkyl group occur: for alkyl groups substituted to a C atoms, the value of B_1 is > 200 J kg mol^{-2} greater than for an analogical group substituted to an N atom:

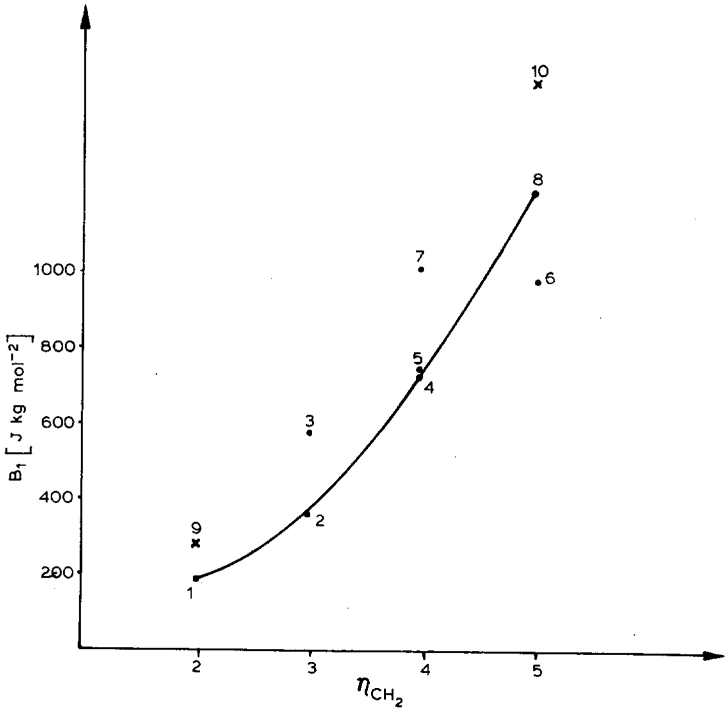

Fig. 2. Coefficient B_1 vs. number of CH_2 groups of diluted aqueous solutions at 313.15 K for: (1) *N*-methylacetamide; (2) *N*-ethylacetamide; (3) *N*-methylpropionamide; (4) *N*-propylacetamide; (5) *N*-*i*-propylacetamide; (6) *N*-*t*-butylacetamide; (7) *N*-methylisobutyramide; (8) *N*-butylacetamide; and at 298.15 K for: (9) *N*-methylacetamide; (10) *N*-butylacetamide.

C_2H_5–NH–CO–CH_3, B_1 = 362.1; CH_3–NH–CO–C_2H_5, B_1 = 570.2; $(CH_3)_2$CH–NH–CO–CH_3, B_1 = 748.6; CH_3–NH–CO–CH$(CH_3)_2$, B_1 = 1009.7 (Table 2).

On the basis of experimental data (Table 1) the association model of Stroesser and Gill [10] was used for the calculations. These calculations did not give positive results.

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