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THERMODYNAMIC EXCESS FUNCTIONS OF DILUTED AQUEOUS SOLUTIONS OF ALKYLATED PYRIMIDINES AND AMINO PURINES, AND CAFFEINE

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ABSTRACT

Heats of dilution data for 1,3-dimethyluracil, 1,3,6-trimethyluracil, 1,3-dimethylthymine, 1,3-diethylthymine, 2-methylamino-9-methylpurine, 6-dimethylamino-9-methylpurine and caffeine, and total pressure data for 1,3-dimethyluracil, 1,3,6-trimethyluracil and 1,3-diethylthymine diluted aqueous mixtures are reported. The results are correlated by means of the NRTL equation. The ability of this equation to represent the thermodynamic functions of diluted mixtures of alkylated nucleic acid–base water mixtures is discussed.

INTRODUCTION

Model compounds, bearing the molecular structure of nucleic acid segments, provide a means of investigating of the molecular features that contribute to the structural stability of these acids in aqueous solutions. Knowledge of such systems is poor and there is a need for more results, especially for simple model systems suitable for explanation of the solution behavior.

The purpose of the present paper, one of a series [1] on the thermodynamics of solute–solvent interactions in dilute aqueous solutions of nucleic acid-base mixtures, was to determine the thermodynamic excess properties and provide an adequate description of these solutions. Caffeine and alkylated derivatives of uracil, thymine (1,3-dimethyluracil, 1,3,6-trimethyluracil, 1,3-dimethylthymine and 1,3-diethylthymine) and amino purine (2-methylamino-9-methylpurine and 6-dimethylamino-9-methylpurine) were chosen as model compounds.

In the reported investigations of solute–solvent interactions, the thermodynamic properties are usually discussed in the form of apparent molar values, as functions of solution molalities, a tedious form for thermodynamic computations. In this paper an effort is made to obtain an exact description of the investigated systems in terms of excess properties, calculated from experimental heats of dilution (Q) and total pressure data.

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An effort was made to correlate the results by means of the NRTL equation and its proposed modifications, making allowances for association and solvation effects [2]. This was justified by the well-known good performance of this model in the representation of excess chemical potentials at infinite dilution, even for the systems forming two liquid phases at higher concentrations.

EXPERIMENTAL

Materials

The substances used were supplied by the Institute of Biochemistry and Biophysics, Warsaw [1]. The purity was checked by the cryometric method (CM) [3] or by gas–liquid chromatography (GLC). The heats of fusion (H_f) and melting temperatures were determined with the use of a DCM-2 differential scanning microcalorimeter calibrated with indium and tin standards. This calibration was checked using benzoic acid standard containing 99.98 mole% of pure component. The obtained value, $H_f = 18.21 \pm 0.61$ kJ mol^{-1}, corresponds well with the value $H_f = 18.00 \pm 0.10$ kJ mol^{-1} reported for benzoic acid by Furukawa et al. [4]. The results obtained are reported in Table 1.

Heat of dilution

The measurements were made at 298.05 ± 0.01 K, 207.89 ± 0.01 K and 317.75 ± 0.02 K in a batch microcalorimeter (LKB 10700-2). A solution of known mass and composition was placed in the calorimetric vessel and known masses of water were then introduced stepwise to the vessel. The heat of dilution, $Q(x_1', x_1'')$, representing the change of the solution enthalpy with the change of solution concentration from mole fraction x_1' to x_1'', was measured for each step. Qualitative results for solutions containing uracil and thymine derivatives were reported graphically elsewhere [1], quantitative data are given in Table 2. The measured accuracy of heat effects was ± 0.02 J mol^{-1} and of concentration ± 0.0002 mole%.

Total pressure

The ebulliometric method proposed for determination of activity coefficients at infinite dilution, γ_i^{∞}, and described elsewhere [5] was used. The measurements were made for the aqueous solutions of 1,3-dimethyluracil, 1,3,6-trimethyluracil and 1,3-dimethylthymine in the concentration range 0–0.007 mole fraction of these compounds (x_1) at constant temperature T(K) = 313.167, with calibration accuracy ± 0.004 and fluctuations lower than 0.0005 K. The obtained total pressure values (P_{exp}) listed in Table 3

TABLE 1

Properties of pure substances

Substance	Content of impurities (mole%)	Molar volume ($cm^3\ mol^{-1}$)	Melting temp. (K)		H_f ($kJ\ mol^{-1}$)	Hypothetical vapour pressure at 313.18 K (Pa)
			Obsd.	Lit.		
1,3-Dimethyluracil	0.14 ± 0.04	111.8	392.5	393	23.1 ± 0.8	155
1,3,6-Trimethyluracil	0.21 ± 0.06	124.3	384.5	385	21.2 ± 0.4	535
1,3-Dimethylthymine	0.3 ± 0.1	122.1	426.5	428	23.6 ± 0.7	4385
1,3-Diethylthymine	0.3 ± 0.1	158.5	327.0	327	21.6 ± 1.4	
2-Methylamino-9-methylpurine	0.4 ± 0.1 [a]	135.3				
6-Dimethylamino-9-methylpurine	0.4 ± 0.1 [a]	146.3				
Caffeine	0.4 ± 0.1 [a]	157.9				

[a] Manufacturer's claim.

TABLE 2

Experimental values of heat of dilution $[Q(x_1^{i'}, x_1^{i''})]$ from mole fraction $x_1^{i'}$ to $x_1^{i''}$ and excess chemical potential μ^E of compounds in water at temperature T

T(K) = 298.05				T(K) = 307.89				T(K) = 317.75			
i	x_1^i	$Q(x_1^{i'}, x_1^{i''})$	μ^E	i	x_1^i	$Q(x_1^{i'}, x_1^{i''})$	μ^E	i	x_1^i	$Q(x_1^{i'}, x_1^{i''})$	μ^E
		(J mol^{-1})				(J mol^{-1})				(J mol^{-1})	
1,3-Dimethyluracil											
1	0.031953		−522.6	1	0.025110		−415.8	1	0.025102		−297.3
		−0.036				−1.088				−1.789	
2	0.020150		−537.2	2	0.016180		−421.3	2	0.016214		−296.6
		−0.475				−0.937				−1.244	
3	0.012870		−546.4	3	0.010370		−424.9	3	0.010737		−296.2
		−0.423				−0.599				−0.813	
4	0.008664		−551.8	4	0.006870		−427.1	4	0.007034		−296.2
		−0.334				−0.327				−0.462	
5	0.005697		−555.7	5	0.004960		−428.3	5	0.004678		−295.8
		−0.178				−0.228				−0.245	
6	0.003768		−558.2	6	0.003300		−429.3	6	0.003154		−295.7
		−0.106				−0.123				−0.122	
7	0.002485		−559.9	7	0.002170		−430.0	7	0.002098		−295.6
		−0.049				−0.062				−0.052	
8	0.001647		−561.0	8	0.001430		−430.5	8	0.001427		−295.6
		−0.025				−0.023					
9	0.001096		−561.7	9	0.000960		−430.8				
1,3,6-Trimethyluracil											
1	0.059798		−1283.4	1	0.038228		−889.8	1	0.056708		−919.0
		2.700				−1.659				−1.681	
2	0.040072		−1281.3	2	0.026537		−917.7	2	0.038350		−961.2
		−0.302				−2.055				−2.921	
3	0.027595		−1280.2	3	0.018770		−936.9	3	0.026827		−988.9
		−1.182				−1.866				−2.898	
4	0.019590		−1279.5	4	0.013435		−950.3	4	0.018893		−1008.6
		−1.374				−1.511				−2.510	
5	0.013909		−1279.1	5	0.009710		−959.8	5	0.013552		−1022.1
		−1.266				−1.168				−1.902	
6	0.009799		−1278.9	6	0.006999		−966.8	6	0.009494		−1032.5
		−0.972				−1.818				−1.384	
7	0.007000		−1279.7	7	0.005078		−971.8	7	0.006782		−1039.5
		−0.691				−0.528				−0.920	
8	0.005085		−1278.6	8	0.003775		−975.2	8	0.004862		−1044.5
		−0.481				−0.362				−0.605	
9	0.003701		−1278.5	9	0.002779		−977.8	9	0.003501		−1048.1
		−0.314				−0.233				−0.385	
10	0.002679		−1278.4	10	0.002042		−979.7	10	0.002501		−1050.7
		−0.197				−0.137				−0.201	
11	0.001933		−1278.4	11	0.001497		−981.1	11	0.001794		−1052.6
		−0.116				−0.080				−0.121	
12	0.001387		−1278.4	12	0.001110		−982.2	12	0.001304		−1053.8
		−0.065				−0.045				−0.070	
13	0.000995		−1278.3	13	0.000811		−982.9	13	0.000948		−1054.8
		−0.031				−0.031				−0.037	
14	0.000722		−1278.3	14	0.000591		−983.5	14	0.000691		−1055.5
		−0.011				−0.060					
15	0.000531		−1278.3	15	0.000432		−983.9	15			

1,3-Dimethylthymine

1	0.008126		−889.4	1	0.008028		−968.4	1	0.008565		−1034.5
2	0.005791	−0.726	−898.4	2	0.005814	−0.883	−967.4	2	0.006084	−1.183	−1033.4
3	0.004217	−0.518	−897.7	3	0.004195	−0.661	−966.7	3	0.004463	−0.767	−1032.8
4	0.003098	−0.371	−897.2	4	0.003088	−0.412	−966.3	4	0.003237	−0.546	−1032.2
5	0.002271	−0.247	−896.9	5	0.002264	−0.293	−965.9	5	0.002266	−0.369	−1031.8
6	0.001679	−0.152	−896.6	6	0.001651	−0.190	−965.7	6	0.001645	−0.201	−1031.6
7	0.001235	−0.092	−896.4	7	0.001210	−0.108	−965.5	7	0.001185	−0.114	−1031.4
8	0.000903	−0.058	−896.3	8	0.000873	−0.060	−965.3	8	0.000847	−0.066	−1031.2
9	0.000654	−0.032	−896.2	9	0.000615	−0.028	−965.2	9	0.000616	−0.033	−1031.1
10	0.000485	−0.015	−896.1	10	0.000448	−0.016	−965.1	10	0.000447	−0.011	−1031.1
				11	0.000326	−0.012	−965.1				

1,3-Diethylthymine

1	0.011576		−1624.0	1	0.020694		−1439.1	1	0.021071		−1457.6
2	0.007427	4.343	−1710.8	2	0.013100	11.504	−1568.9	2	0.013338	9.660	−1574.7
3	0.004887	1.660	−1766.0	3	0.008452	4.744	−1653.5	3	0.008640	3.687	−1650.0
4	0.003194	0.629	−1803.7	4	0.005481	1.830	−1709.7	4	0.005658	1.305	−1699.6
5	0.002136	0.210	−1827.7	5	0.003579	0.629	−1746.7	5	0.003746	0.402	−1732.2
6	0.001428	0.070	−1843.9	6	0.002373	0.193	−1770.5	6	0.002453	0.101	−1754.5
7	0.000951	0.023	−1854.9	7	0.001561	0.052	−1786.7	7	0.001620	−0.003	−1769.0
				8	0.001048	0.005	−1797.0	8	0.001083	−0.009	−1778.5
								9	0.000717	−0.006	−1784.9

2-Methylamino-9-methylpurine

1	0.000445		−2950.9	1	0.000569		−2667.7	1	0.000560		−2497.8
2	0.000329	−0.365	−2951.3	2	0.000420	−0.451	−2668.0	2	0.000420	−0.379	−2498.0
3	0.000243	−0.242	−2951.5	3	0.000311	−0.286	−2668.2	3	0.000313	−0.230	−2498.2
4	0.000179	−0.151	−2951.7	4	0.000230	−0.167	−2668.4	4	0.000234	−0.146	−2498.3
5	0.000131	−0.088	−2951.9	5	0.000168	−0.097	−2668.5	5	0.000177	−0.085	−2498.4
6	0.000095	−0.051	−2952.0	6	0.000125	−0.054	−2668.6	6	0.000131	−0.062	−2498.5
7	0.000072	−0.022	−2952.1	7	0.000092	−0.023	−2668.7	7	0.000095	−0.030	−2498.5
8	0.000053	−0.013	−2952.2	8	0.000068	−0.012	−2668.8	8	0.000069	−0.018	−2498.6
9	0.000040	−0.007	−2952.2	9	0.000050	−0.008	−2668.8	9	0.000050	−0.009	−2498.6
10	0.000030	−0.001	−2952.2	10	0.000037	−0.005	−2668.8				

TABLE 2 (continued)

T(K) = 298.05				T(K) = 307.89				T(K) = 317.75			
i	x_1^i	$Q(x_1^{i'}, x_1^{i''})$	μ^E	i	x_1^i	$Q(x_1^{i'}, x_1^{i''})$	μ^E	i	x_1^i	$Q(x_1^{i'}, x_1^{i''})$	μ^E
		(J mol^{-1})				(J mol^{-1})				(J mol^{-1})	
6-Dimethylamino-9-methylpurine											
1	0.000956		−5630.5	1	0.001134		−4735.5	1	0.001176		−5195.5
		−1.107				−1.331				−1.508	
2	0.000689		−5666.6	2	0.000882		−4739.4	2	0.000885		−5201.4
		−0.825				−1.029				−1.120	
3	0.000498		−5692.6	3	0.000595		−4743.8	3	0.000631		−5206.6
		−0.609				−0.773				−0.850	
4	0.000350		−5711.5	4	0.000432		−4746.4	4	0.000462		−5210.0
		−0.487				−0.568				−0.636	
5	0.000262		−5725.0	5	0.000315		−4748.2	5	0.000338		−5212.5
		−0.364				−0.418				−0.449	
6	0.000191		−5734.8	6	0.000229		−4749.6	6	0.000246		−5214.4
		−0.257				−0.294				−0.299	
7	0.000140		−5741.8	7	0.000166		−4750.6	7	0.000181		−5215.7
		−0.187				−0.183				−0.196	
8	0.000102		−5747.1	8	0.000120		−4751.3	8	0.000133		−5216.7
		−0.126				−0.130				−0.127	
9	0.000074		−5751.0	9	0.000087		−4751.8	9	0.000097		−5217.4
		−0.081				−0.084				−0.077	
10	0.000054		−5753.8	10	0.000063		−4752.2	10	0.000069		−5218.0
		−0.051				−0.042				−0.036	
11	0.000039		−5755.8	11	0.000047		−4752.4	11	0.000051		−5218.3
		−0.027				−0.025				−0.017	
12	0.000028		−5757.4	12	0.000033		−4752.6	12	0.000038		−5218.6
		−0.014				−0.013					
13	0.000020		−5758.5	13	0.000023		−4752.8				
						−0.009					
				14	0.000017		−4752.9				
						−0.005					
				15	0.000013		−4752.9				
Caffeine											
1	0.000852		−1777.5	1	0.000939		−1809.3	1	0.000937		−1793.3
		−0.352				−0.397				−0.405	
2	0.000632		−1777.6	2	0.000697		−1809.4	2	0.000695		−1793.4
		−0.245				−0.276				−0.256	
3	0.000467		−1777.6	3	0.000520		−1809.4	3	0.000517		−1793.4
		−0.159				−0.181				−0.179	
4	0.000346		−1777.7	4	0.000386		−1809.5	4	0.000380		−1793.5
		−0.102				−0.115				−0.102	
5	0.000255		−1777.7	5	0.000288		−1809.5	5	0.000282		−1793.5
		−0.061				−0.073				−0.068	
6	0.000186		−1777.7	6	0.000216		−1809.5	6	0.000210		−1793.5
		−0.033				−0.046				−0.041	
7	0.000139		−1777.7	7	0.000159		−1809.5	7	0.000155		−1793.5
		−0.019				−0.022				−0.027	
8	0.000102		−1777.7	8	0.000119		−1809.5	8	0.000113		−1793.5
		−0.010				−0.015				−0.013	
9	0.000075		−1777.7	9	0.000089		−1809.6	9	0.000083		−1793.5
						−0.007					
				10	0.000065		−1809.6				

TABLE 3

Total pressure (P) of aqueous mixtures of pyrimidines

Mole fraction of pyrimidine x_1	Total pressure P_{exp}(Pa)	$(P_{lin} - P_{exp})$(Pa)	$(P_{NRTL} - P_{exp})$(Pa)
1,3-Dimethyluracil			
0.0000	7366	−2.7	–
0.0013	7354	0.0	2.6
0.0024	7347	−1.3	1.3
0.0034	7338	1.3	3.4
0.0044	7330	2.6	4.1
0.0055	7321	4.0	5.4
0.0065	7317	0.0	2.2
0.0075	7314	−4.0	−2.4
RMSD(P)		2.5	3.3
1,3,6-Trimethyluracil			
0.0000	7366	−0.6	–
0.0009	7359	−0.3	0.4
0.0017	7354	−0.6	0.1
0.0033	7339	2.9	3.5
0.0043	7335	−0.1	0.4
0.0060	7325	−1.3	−1.0
RMSD(P)		1.3	1.6
1,3-Diethylthymine			
0.0000	7366	1.1	–
0.0011	7363	−1.9	−3.1
0.0024	7354	0.7	−0.6
0.0034	7349	0.8	−0.6
0.0053	7341	−1.0	−2.9
0.0064	7334	0.0	−2.2
0.0076	7327	0.4	−2.1
RMSD(P)		1.0	2.2

were fitted by the least-squares method with the linear equation

$$P_{lin} = P^0_{H_2O} + ax_1 \quad (1)$$

where a is an adjustable parameter, and $P^0_{H_2O}$ is the vapour pressure of pure water.

The obtained values of $P^0_{H_2O}$ and a are given together with correlation coefficients in Table 4.

CORRELATION AND PREDICTION

Heat of dilution $[Q(x_1^{i'}, x_1^{i''})]$ of the solution from solute 1 concentration $x_1^{i'}$ to $x_1^{i''}$ represents the difference of excess enthalpy H^E at concentration $x_1^{i'}$,

TABLE 4

Computed constants of eqn. (1)

Substance	$P^0_{H_2O}$(Pa)	a(Pa)	Correlation coefficient
1,3-Dimethyluracil	7363	7209	0.991
1,3,6-Trimethyluracil	7366	7002	0.996
1,3-Diethylthymine	7367	5172	0.997

and at concentration $x_1^{i''}$

$$Q\left(x_1^{i'}, x_1^{i''}\right) = H^{\mathrm{E}}|_{x_1^{i'}} - H^{E}|_{x_1^{i''}} \tag{2}$$

H^{E} at given temperature T can be computed from the measured values of heat of dilution only on assumption that a model reproducing H^{E} as function of mixture composition at the same T is known. The NRTL equation is frequently used [6,7] for this purpose, possessing the advantage of simultaneous representation of excess Gibbs energy (G^{E}) and H^{E}. For a binary mixture the following form of the NRTL equation is used

$$G^{\mathrm{E}} = RTx_1x_2\left[\frac{\tau_{12}G_{12}}{x_1 + x_2G_{12}} + \frac{\tau_{21}G_{21}}{x_2 + x_1G_{21}}\right] \tag{3}$$

where

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} \tag{4}$$

$$G_{ij} = \exp(-\alpha\tau_{ij}) \tag{5}$$

where α, $(g_{ij} - g_{jj})$ are adjustable parameters, and subscripts 1 and 2 refer to the solute and water, respectively. Equation [3] can be rearranged to represent H^{E} according to the Gibbs–Helmholtz relation

$$H^{\mathrm{E}} = G^{\mathrm{E}} - T\frac{\partial G^{\mathrm{E}}}{\partial T} \tag{6}$$

For this purpose equations relating the adjustable parameters to T are necessary. A linear dependence of parameters from T was given for this purpose by Renon et al. [8]. As good results were obtained using eqn. (4) for the temperature dependence of the NRTL equation parameters [6,7] and due to the small T interval, the last method was chosen. The α parameter was fixed at -1, following the recommendation of Marina and Tassios [9].

The computed values of NRTL parameters are given in Table 5 together with root mean square deviations of heat of dilution (RMSD Q) computed according to

$$\mathrm{RMSD}(Q) = \sqrt{\frac{\left(Q_{\mathrm{NRTL}} - Q_{\mathrm{exp}}\right)^2}{n}} \tag{7}$$

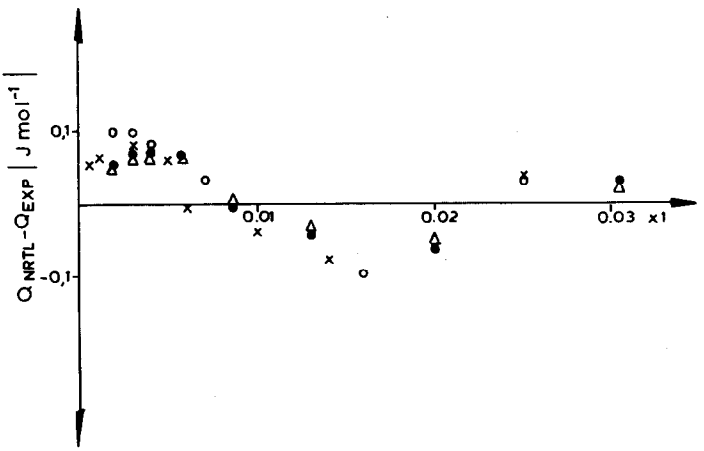

Fig. 1. Plot of deviations of calculated and experimental values of heat of dilution calculated by means of the NRTL equation with two adjustable parameters [eqn. (3)] at: 298.05 K (●); 307.89 K (×), and 317.75 K (○). △ = Deviations of values calculated by means of the NRTL equation with four adjustable parameters (NRTLMK).

TABLE 5

Parameters of the NRTL equation of aqueous solutions calculated from heat of dilution measurements (parameter $\alpha = -1$) and limiting values of chemical potentials μ_1^∞ at temperature T

Solute (1)	T(K)	$G_{12} - G_{22}$ (J mol^{-1})	$G_{21} - G_{11}$ (J mol^{-1})	RMSD(Q)	μ_1^∞
1,3-Dimethyluracil	298.05	845.94	−1753.27	0.034	−563
	307.89	689.95	−1334.78	0.060	−431
	317.75	−524.56	134.62	0.074	−295
1,3,6-Trimethyluracil	298.05	923.65	−2315.37	0.081	−974
	307.89	893.69	−2252.22	0.101	−985
	317.75	879.91	−2284.98	0.162	−1057
1,3-Dimethylthymine	298.05	−1698.88	−40.01	0.032	−896
	307.89	−1702.44	−89.49	0.047	−965
	317.75	−1712.52	−135.28	0.068	−1031
1,3-Diethylthymine	298.05	1508.27	−4649.11	0.016	−1877
	307.89	1518.44	−4566.18	0.044	−1818
	317.75	1511.15	−4475.11	0.036	−1798
2-Methylamino-9-methylpurine	298.05	−987.67	−2289.32	0.036	−2952
	307.89	−978.99	−2001.04	0.050	−2669
	317.75	−1096.41	−1774.66	0.042	−2499
6-Dimethylamino-9-methylpurine	298.05	1071.37	−7412.11	0.019	−5761
	307.89	−1015.56	−4070.16	0.092	−4753
	317.75	−1016.26	−4527.64	0.059	−5219
Caffeine	298.05	−1187.15	−1042.48	0.029	−1778
	307.89	−1162.16	−1071.22	0.031	−1809
	317.75	−1206.77	−1029.27	0.035	−1794

TABLE 6

Relative root mean square deviations (RMSD) of Q; data reduction using the NRTL

Substance	No. of pts.	T(K)	NRTL		Eqn. (8)	
			Parameter No.	RMSD	Parameter No.	RMSD
1,3-Dimethyl-uracil	8	298.05	2	10.1	2	32.8
	8	307.89	2	5.5	2	5.6
	7	317.75	2	4.1	2	11.2
1,3,6-Trimethyl-uracil	14	298.05	2	3.0	2	49.7
	14	307.89	2	4.9	2	31.9
	13	317.75	2	5.5	2	40.3
1,3-Dimethyl-thymine	9	298.05	2	4.4	2	8.7
	10	307.89	2	5.3	2	6.7
	9	317.75	2	5.7	2	2.2
1,3-Diethyl-thymine	6	298.05	2	0.4	2	3.6
	7	307.89	2	0.4	2	5.3
	8	317.75	2	0.4	2	5.6
2-Methylamino-9-methylpurine	9	298.05	2	9.9	2	3.2
	9	307.89	2	11.0	2	3.8
	8	317.75	2	11.1	2	3.2
6-Dimethylamino-9-methylpurine	12	298.05	2	1.8	2	41.6
	14	307.89	2	6.9	2	27.5
	11	317.75	2	3.9	2	21.3
Caffeine	8	298.05	2	8.4	2	2.0
	9	307.89	2	7.8	2	3.5
	8	317.75	2	8.7	2	5.1

where n is the number of experimental points, and subscripts NRTL and exp denote computed and measured values, respectively.

The heat of dilution of 1,3-dimethyluracil residuals are plotted against mole fraction (Fig. 1). The values of deviations are small, but exhibit some systematic deviations similar at all temperatures. This situation is typical for all considered substances and shows that the flexibility of the NRTL equation is insufficient. Other equations were tested. The results were similar to these obtained by means of NRTL with three adjustable parameters, UNIQUAC and NRTL with provisions for association according to the Mecke–Kempter model (NRTLMK) as proposed by Gierycz [2]. In Fig. 1 the residuals of heat of dilution are plotted for the Gierycz model. The deviations are smaller but still bear the same concentration dependence.

A comparison of total pressure values calculated using the NRTL equa-

equation and eqn. (8) with a variable number of adjustable parameters

Parameter No.	RMSD	Parameters of eqn. (8) B_1	B_2	B_3	B_4	B_5
3	28.4	−142.06	93.74	−20.35		
3	3.5	−291.89	257.33	−88.37		
3	4.0	−316.46	222.83	−62.34		
5	8.0	−736.05	827.46	−483.14	137.78	−14.83
5	2.2	−916.87	1216.98	−947.09	382.83	−60.68
5	4.2	−888.83	915.83	−526.39	151.88	−16.80
4	1.4	−1064.49	2181.50	−2551.79	1275.13	
3	2.7	−1108.93	1775.81	−1230.77		
3	0.9	−1146.58	1616.22	−977.79		
3	0.9	137.03	1009.82	−711.38		
3	2.0	140.57	557.46	−266.44		
4	0.7	−219.59	1264.52	−1146.79		
4	1.6	Unreasonable values				
4	2.8	Unreasonable values				
4	1.9	Unreasonable values				
5	4.7	Unreasonable values				
5	3.8	Unreasonable values				
5	4.3	Unreasonable values				
3	1.6	−25468.9	229514.8	−828593.2		
3	3.2	−25109.9	227159.3	−901337.1		
3	2.3	−26693.8	325954.6	−2113608.6		

tion in its simplest form ($\alpha = -1$) with the experimental values shows that this equation represents satisfactorily the thermodynamic properties of dilute solutions of pyrimidines and can be used to represent properties of aqueous solutions of alkylated nucleic acid–base mixtures.

For further comparison the correlation of Q by means of two constants for the NRTL equation and for eqn. (8) used by Savage and Wood [10] was made

$$Q = \sum_{j=1}^{k} B_j \left(m_{A_i}^j - m_{B_i}^j \right) \tag{8}$$

where m_{A_i} is the molality of solution before dilution No. i; m_{B_i} is the molality of solution after dilution No. i; B_i is an adjustable parameter; and k is the number of adjustable parameters.

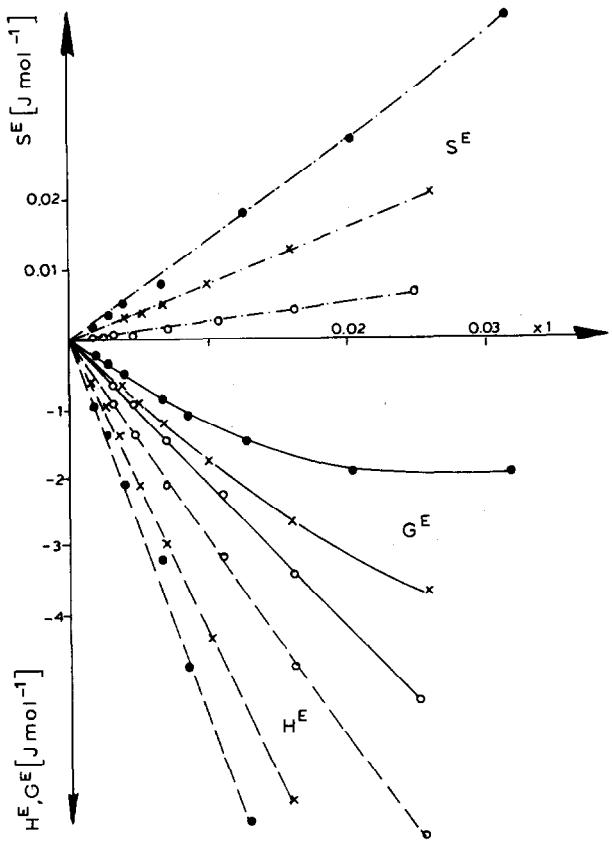

Fig. 2. Excess thermodynamic properties of diluted mixtures of 1,3-dimethyluracil at: 298.05 K (●), 307.89 K (×), and 317.75 K (○).

In eqn. (8) molalities are used as concentration units; in NRTL equations mole fractions are used. Consequently, heat of dilution is calculated per 1 mole of solute in the former case and per 1 mole of mixture in the latter. For a comparison of the results the root mean square deviations (RMSD) were calculated for both methods according to

$$\mathrm{RMSD} = 100 \sqrt{\frac{\sum_{i=1}^{n} \frac{\left(Q_{\mathrm{exp}}^{(i)} - Q_{\mathrm{calc}}^{(i)}\right)^2}{Q_{\mathrm{exp}}^{(i)}}}{n-k}} \tag{9}$$

where n is the number of dilution experiments, and k is the number of adjustable parameters. Subscripts exp and calc indicate measured and computed values from the equation, respectively. The RMSD values computed according to this formula can be directly compared.

A comparison of the correlation by eqn. (8) and the NRTL equations

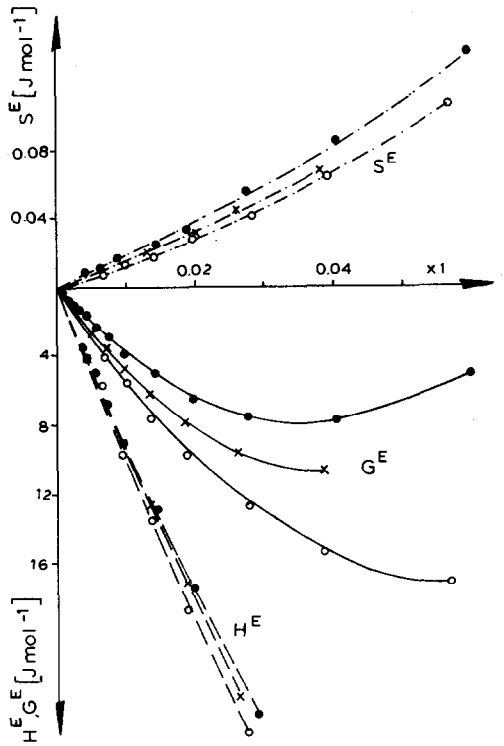

Fig. 3. Excess thermodynamic properties of diluted mixtures of 1,3,6-trimethyluracil at 298.05 K (●), 307.89 K (×), and 317.75 K (○).

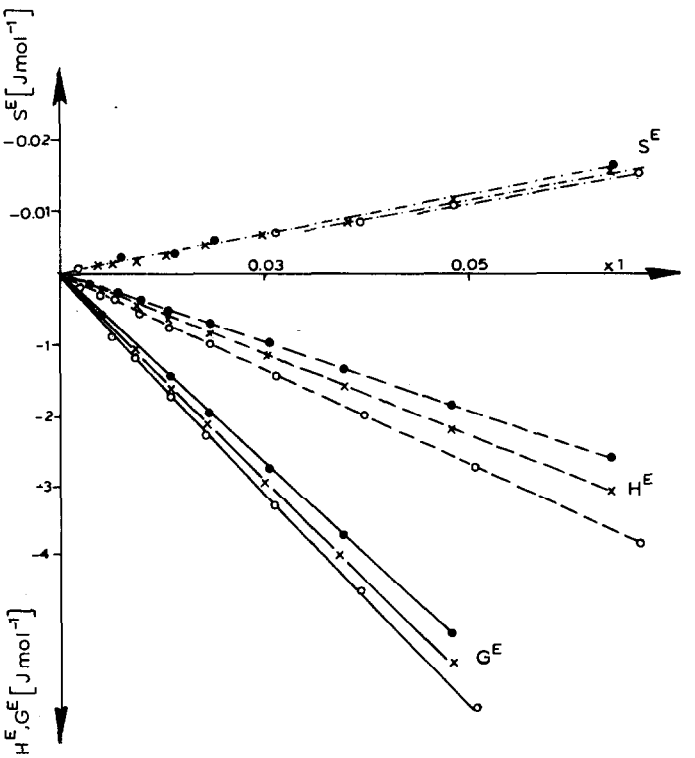

Fig. 4. Excess thermodynamic properties of diluted mixtures of 1,3-dimethylthymine at 298.05 K (●), 307.89 K (×), and 317.75 K (○).

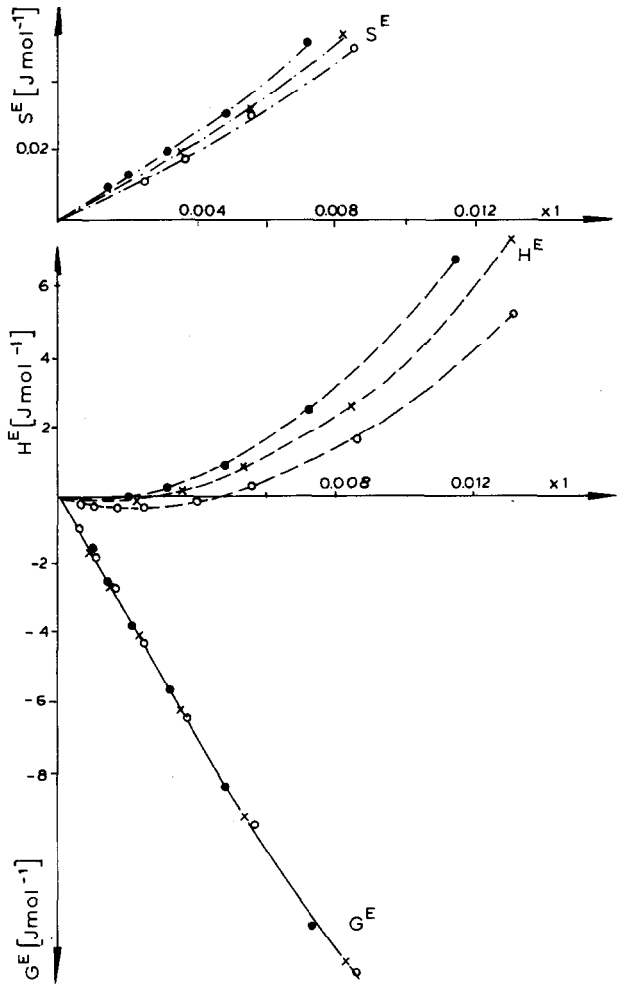

Fig. 5. Excess thermodynamic properties of diluted mixtures of 1,3-diethylthymine at 298.05 K (●), 307.89 K (×), and 317.75 K (○).

(3)–(6) is given in Table 6. The correlation results for the same number of adjustable parameters are always much better except for 2-methylamino-9-methylpurine, but in this case the obtained absolute values of parameters were higher than 10^6 and due to this better fit can be treated as accidental. In general, in order to obtain a similar performance using eqn. (8) to that achieved by the NRTL equation with two adjustable parameters, three to five adjustable parameters are necessary. In addition, the NRTL equation produces simultaneously information regarding other thermodynamic properties of mixtures, such as S^E and G^E.

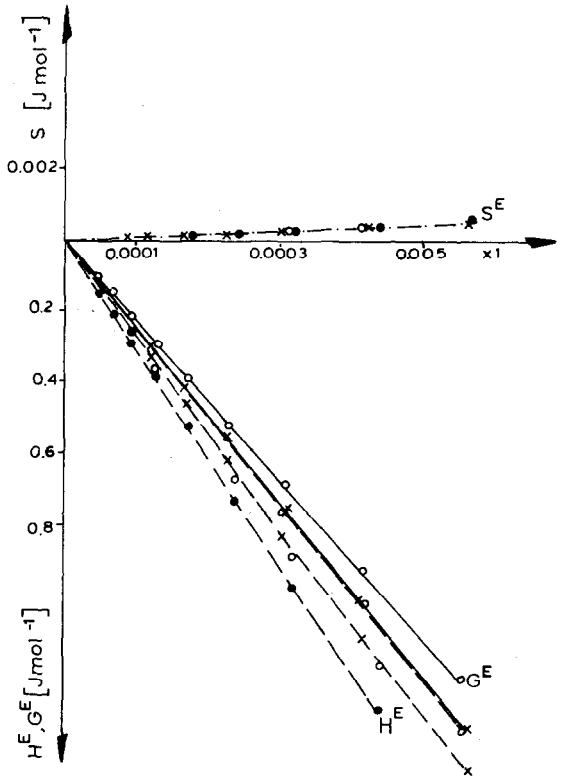

Fig. 6. Excess thermodynamic properties of diluted mixtures of 2-methylamino-9-methylpurine at 298.05 K (●), 307.89 K (×), and 317.75 K (○).

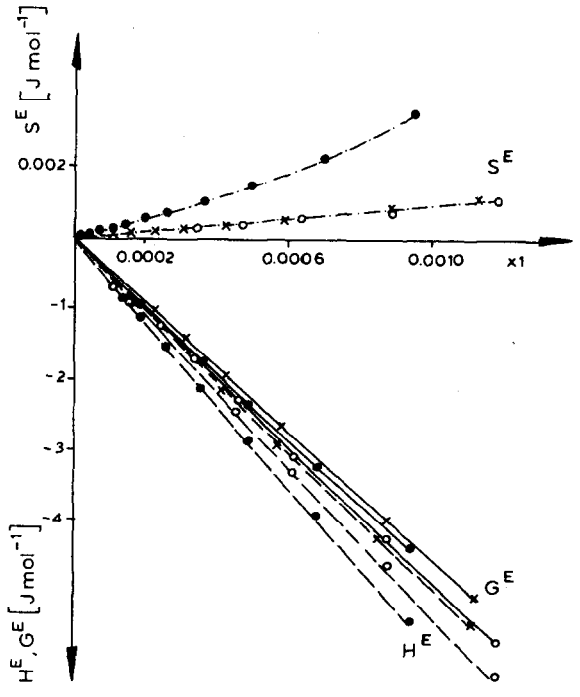

Fig. 7. Excess thermodynamic properties of diluted mixtures of 6-dimethylamino-9-methylpurine at 298.05 K (●), 307.89 K (×), and 317.75 K (○).

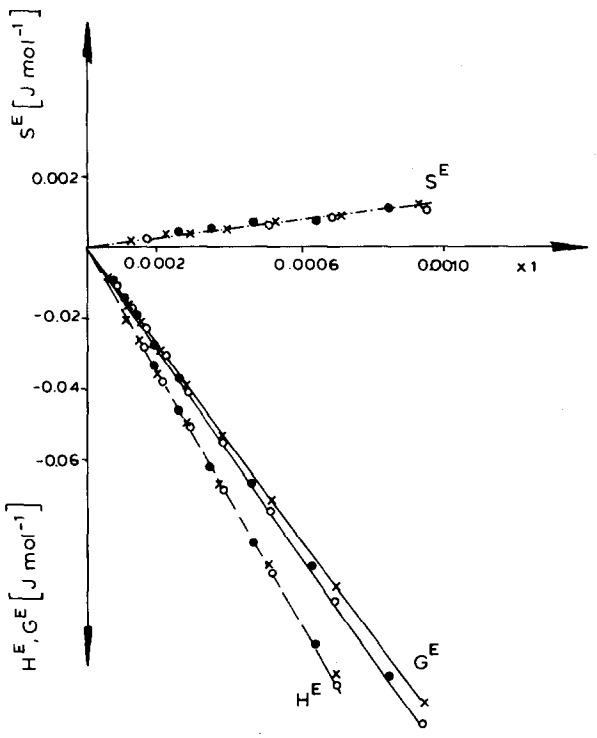

Fig. 8. Excess thermodynamic properties of diluted mixtures of caffeine at 298.05 K (●), 307.89 K (×), and 317.75 K (○).

CONCLUSIONS

The H^E, G^E and excess entropy S^E of the investigated compounds are presented in Figs. 2–8. As can be seen from the figures, at low concentration all mixtures have negative values of H^E and G^E and positive values of S^E. The G^E values of uracils become positive with increase in concentration. The H^E values of 1,3-diethylthymine became negative at very low concentrations.

To characterize the mixtures of infinite dilution the values of excess chemical potential, μ_1^E, at infinite dilution are given in Table 5. In order to visualize the behaviour of the investigated compounds in mixtures, computed values of μ^E are reported at different concentrations in Table 2.

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