Limiting Partial Molar Excess Enthalpies of Selected Organic Compounds in Water at 298.15 K

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A flow mixing microcalorimeter in conjunction with asymmetric syringe-type pumps was employed to measure enthalpies of mixing at 298.15 K for highly dilute aqueous solutions of 16 organic solvents of moderate hydrophobicity. Limiting partial molar excess enthalpies were determined by extrapolating these data to infinite dilution. Except for 2,4-pentanedione, the values of limiting partial molar excess enthalpies for all the examined mono- and bifunctional compounds containing hydroxy, keto, ether, ester, and nitrile groups are negative, indicating that the process of their dissolution in water is energetically favored at room temperature. Comparison with available literature data showed good agreement. Prediction of limiting partial molar excess enthalpies was tested for two group-contribution methods: that of Cabani et al. (*J. Solution Chem*. **1981**, *10*, 563−595) was found to be fairly good for monofunctional derivatives, but failed for the bifunctional derivatives, and the modified UNIFAC (Dortmund) yielded completely unsatisfactory results.

Introduction

During past decades, phase partitioning of organic compounds in dilute aqueous solutions has been extensively studied, being required for environmental pollution control, chemical technology, food technology, and biotechnology applications and stimulated by the theoretical interest of solution thermodynamics and biochemistry. Importance of the temperature dependence of the partition phenomena for these applications has been well-recognized, inciting experimental effort to determine related thermal properties.

In this work, which is a part of a broader project, we determine the limiting partial molar excess enthalpies at infinite dilution in water by flow-mixing calorimetry for selected mono- and bifunctional semihydrophobic compounds containing hydroxy, keto, ether, ester, and nitrile groups. The selected compounds are important industrial solvents and potential environmental pollutants. We compare the results to literature values and examine the performance of two group-contribution prediction methods, namely, that of Cabani et al.[1] and the modified UNIFAC (Dortmund)[2−5] against the measured data.

The enthalpic data obtained in this work complement the results of our measurements of gas−liquid partitioning and partial molar excess heat capacities at infinite dilution, which have been carried out for the same set of compounds and reported in specialized papers.[6,7] Reliable determination of the temperature dependence of the limiting activity coefficient, a key thermodynamic quantity governing fluid-phase equilibria in dilute solutions, has been in turn achieved by simultaneous thermodynamic treatment of all the available information.[6]

Experimental Section

Materials. Organic compounds used as solutes in addition to their source and purity are specified in Table 1. Water used as the solvent was deionized and degassed under vacuum prior use.

Apparatus and Procedure. Mixing enthalpies of highly dilute solutions as the primary data for determination of limiting partial molar excess enthalpies, $\bar{H}_1^{E,\infty}$, were measured with a modified LKB differential microcalorimeter,[8,9] Model 2107-020, operating under constant flow conditions. This classical heat conduction instrument coupled with Gilson HPLC piston pumps has been calibrated by a Joule effect and extensively proved to yield accurate results[10−12] in the conventional composition range ($0.05 < x_1 < 0.95$). Agreement found with reliable literature data for both aqueous and nonaqueous organic systems is mostly better than 0.5% of the maximum thermal effect.[10,11,13] However, at mole fractions lower than 0.05 or higher than 0.95, appreciably higher errors were observed because the symmetric pumping system was incapable of delivering sufficiently stable low flow rates of the minor component. In addition, the pulsing flows of the piston pumps enhanced back diffusion of the major component into the feeding tube of the minor component. Accurate measurements for dilute solutions require an appropriate pumping system. In the present experiments, the components are therefore injected into the calorimeter by two push-syringe units (Razel Scientific Instruments, USA), equipped with special gas syringes (Gastight Models #1002 and #1025, Hamilton, Switzerland). The volumes of the syringes used are 2 and 25 cm^3 for organic compound and water, respectively, to favor the asymmetric flow rates. This pumping system has been employed in our previous study[14] dealing with the determination of limiting partial molar excess enthalpies but in conjunction with a Picker flow calorimeter. Generated at the selected frequencies by the electronic card (Metrabyte CIO-DAS802/16, computer board) inserted into

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10.1021/je020002u CCC: $22.00

Table 1. Organic Solutes Used; Specification of Purity

solute	CAS RN[a]	producer/purity
1-butanol n-C_4H_9−OH	[71-36-3]	Aldrich 99.8% HPLC[b] Fluka >99.5% GC[b]
2-methyl-1-propanol $(CH_3)_2$−CH−CH_2−OH	[78-83-1]	Fluka >99.5% GC[b]
cyclopentanol c-C_5H_9−OH	[96-41-3]	Aldrich 99%[b]
cyclohexanol c-C_6H_{11}−OH	[108-93-0]	Aldrich 99%[b]
2-butanone CH_3−CO−CH_2−CH_3	[78-93-3]	Fluka >99.5% GC[b]
cyclopentanone c-C_5H_8=O	[120-92-3]	Aldrich 99+% GC[b]
cyclohexanone c-C_6H_{10}=O	[108-94-1]	Fluka >99.5% GC[b]
2,4-pentanedione CH_3−CO−CH_2−CO−CH_3	[123-54-6]	Fluka >99.5% GC[c]
methyl acetoacetate CH_3−CO−CH_2−COO−CH_3	[105-45-3]	Aldrich 99+% GC[c]
ethyl acetoacetate CH_3−CO−CH_2−COO−CH_2−CH_3	[141-97-9]	Aldrich 99+%[c]
2-methoxyethyl acetate CH_3−COO−$(CH_2)_2$−O−CH_3	[110-49-6]	Aldrich 99+% HPLC[b]
2-ethoxyethyl acetate CH_3−COO−$(CH_2)_2$−O−CH_2−CH_3	[111-15-9]	Aldrich 99+%[b]
methyl methoxyacetate CH_3−O−CH_2−COO−CH_3	[6290-49-9]	Aldrich 99% GC[b]
acetonitrile CH_3−CN	[75-05-8]	Fluka >99.5% GC[b]
propionitrile CH_3−CH_2−CN	[107-12-0]	Aldrich 99% GC[b]
acrylonitrile CH_2=CH−CN	[107-13-1]	Aldrich 99+%[b,d]

[a] Chemical Abstracts Service registry number. [b] Dried by means of molecular sieves (no further purification). [c] Used directly without any purification or drying. [d] Stabilized (35−45 ppm monomethyl ether hydroquinone).

the computer, two separated lines of square waves are sent to the corresponding step-motor to regulate independently the continuous advance of the piston of each syringe. Accounting for the respective densities of liquids, the flow rates delivered by each pump are adjusted through the software to reach the final composition of the mixture at the desired values, while maintaining constant the total flow rate. The densities of pure components were taken from Hovorka et al.[7] The flow rate of each pump was calibrated by timing and weighing the delivered amount of water or ethylene glycol. The reproducibility of flow rates and their linearity vs frequency was better than 1%. The corresponding uncertainty in the mole fraction inferred using the error propagation law amounts $s(x_1)/x_1 \leq 0.015$. Measurements were carried out at the total flow rate of 0.1 cm^3/min established as optimal during preliminary experiments on the test system of 1-butanol in water. As a viscous solute of limited aqueous solubility, 1-butanol provided a severe check of the suitable setting of experimental parameters, in particular of the residence time in the measuring cell which must be sufficiently long to ensure complete mixing but sufficiently short to minimize back diffusion into the feeding tubes. The tests verified that the proportionality of the calorimeter response was maintained at least up to the total flow rate of 0.25 cm^3/min. Correct performance of the calorimeter was additionally proved by measuring heats of dilution of aqueous 1-butanol solutions; the derived relative enthalpies of solution from the dilution experiments and from the mixing of the pure components exhibited the same composition dependences. Because the thermal effects encountered in dilute-range experiments are small, the signal delivered by thermopiles was multiplied by a factor of 1000 through a differential operational amplifier (homemade) before it was measured with a digital voltmeter (Metrix, Switzerland). An RS232 serial port transferred each reading to the computer program to allow averaging and further calculations. The temperature of the air bath containing the calorimetric unit was controlled to ±0.01 K, the temperature of the block not fluctuating more than 3 mK during a day.

In a typical experimental run, after the baseline signal corresponding to the pure water solvent flow is established, the heat-of-mixing effect is determined for seven compositions approximately in the range $0.01 > x_1 > 0.004$, proceeding from the higher to the lower solute concentration. The limiting partial molar excess enthalpy, $\bar{H}_1^{E,\infty}$, is obtained by extrapolation of the quantity H^E/x_1x_2 as a function of x_1 to infinite dilution. In the dilute region studied, the H^E data exhibit a simple composition dependence, which might be described by the follwing equation

$$\frac{H^E}{x_1x_2} = A + Bx_1 \tag{1}$$

with A being equal to $\bar{H}_1^{E,\infty}$.

Results and Discussion

Excess enthalpies measured for dilute aqueous solutions of 16 semihydrophobic organic compounds are listed in Table 2. No results are presented for methyl acetate, another substance originally involved in the selected set, as for this solute the measurements failed owing to unsurpassable problems with bubble formation in the tubing system. The data listed were typically obtained by merging results from two or three experimental runs. The ample data for 1-butanol resulted from using this solute in test experiments. To evaluate $\bar{H}_1^{E,\infty}$, eq 1 was fitted to experimental data by the weighted least-squares method, as illustrated for ethyl acetoacetate in Figure 1. The weights in the regression were given by standard deviations of signal fluctuations.

The limiting partial molar excess enthalpies are listed in Table 3, together with parameter B of eq 1 that describes the concentration dependence of the measured H^E/x_1x_2 values. Also given in this table are the standard deviations of the least-squares estimates of parameters A and B, $s(A) = s(\bar{H}_1^{E,\infty})$ and $s(B)$, and the dimensionless standard deviation of the fit s. As indicated by roughly unity values of s, the data could be fitted within the level of signal fluctuations, the precision of $\bar{H}_1^{E,\infty}$ determinations from these fits being always better than 1%, except for 2,4-pentanedione (2.5%).

Table 4 presents a comprehensive comparison of our results with data from the literature. No data were found in the literature for six of the examined solutes, namely, the bifunctional derivatives and acrylonitrile. In most cases, the literature data were obtained by an alternative batch calorimetric technique upon minute additions of solute to a bulk of solvent and reported as the enthalpies of solution at infinite dilution. The agreement is good, mostly within 3%, suggesting that the probable total uncertainty of our $\bar{H}_1^{E,\infty}$ determinations lies within this

Table 2. Values of Excess Enthalpies H^E (in the Form H^E/x_1x_2) at 298.15K as a Function of Solute Mole Fraction x_1 for Aqueous Solutions of 16 Organic Solutes Studied

x_1	H^E/x_1x_2 J·mol^{-1}	$s(H^E)/x_1x_2{}^a$ J·mol^{-1}	x_1	H^E/x_1x_2 J·mol^{-1}	$s(H^E)/x_1x_2{}^a$ J·mol^{-1}	x_1	H^E/x_1x_2 J·mol^{-1}	$s(H^E)/x_1x_2{}^a$ J·mol^{-1}	x_1	H^E/x_1x_2 J·mol^{-1}	$s(H^E)/x_1x_2{}^a$ J·mol^{-1}
1-Butanol											
0.00300	−8956	33	0.00600	−8800	25	0.00800	−8629	28	0.01000	−8415	30
0.00300	−8931	29	0.00600	−8790	36	0.00800	−8607	18	0.01000	−8491	28
0.00400	−8893	104	0.00600	−8757	21	0.00800	−8571	39	0.01000	−8414	31
0.00400	−8736	154	0.00600	−8671	24	0.00800	−8589	36	0.01000	−8335	43
0.00400	−8949	68	0.00600	−8694	84	0.00800	−8544	46	0.01000	−8425	33
0.00400	−8868	87	0.00600	−8745	47	0.00800	−8604	36	0.01000	−8392	45
0.00400	−8889	59	0.00600	−8820	107	0.00800	−8592	49	0.01200	−8214	47
0.00400	−8950	136	0.00700	−8703	30	0.00900	−8556	22	0.01200	−8039^b	17
0.00500	−8819	30	0.00700	−8650	30	0.00900	−8563	26	0.01400	−7792^b	48
0.00500	−8867	49	0.00700	−8682	49	0.00900	−8454	53	0.01400	−7247^b	22
0.00500	−8785	90									
2-Methyl-1-propanol											
0.00300	−8949	60	0.00500	−8876	35	0.00700	−8767	26	0.00900	−8565	29
0.00396	−9030	122	0.00594	−8924	65	0.00792	−8757	28	0.00990	−8598	18
0.00400	−8913	64	0.00600	−8782	43	0.00800	−8668	33	0.01000	−8473	34
0.00500	−8840	34	0.00700	−8756	38	0.00900	−8603	36			
Cyclopentanol											
0.00200	−10056	157	0.00600	−9744	52	0.00700	−9699	99	0.00900	−9628	40
0.00300	−9941	111	0.00600	−9801	59	0.00800	−9609	36	0.00900	−9597	48
0.00400	−9886	70	0.00600	−9815	138	0.00800	−9689	50	0.01000	−9443	35
0.00400	−9875	110	0.00700	−9704	44	0.00800	−9555	95	0.01000	−9442	39
0.00500	−9851	67	0.00700	−9758	64	0.00900	−9522	50	0.01000	−9425	49
0.00500	−9821	86									
Cyclohexanol											
0.00120	−8372	271	0.00200	−8297	115	0.00280	−8279	86	0.00360	−8156	80
0.00120	−8355	138	0.00200	−8209	101	0.00280	−8331	81	0.00360	−8185	98
0.00160	−8340	206	0.00240	−8231	98	0.00320	−8266	75	0.00400	−8070	80
0.00160	−8293	121	0.00240	−8285	89	0.00320	−8217	70	0.00400	−8149	88
2-Butanone											
0.00300	−10403	87	0.00500	−10314	38	0.00700	−10167	23	0.00900	−9979	23
0.00400	−10251	61	0.00600	−10195	34	0.00800	−10076	33	0.01000	−9927	84
Cyclopentanone											
0.00350	−8529	42	0.00500	−8450	33	0.00700	−8311	22	0.00900	−8215	17
0.00400	−8423	79	0.00450	−8467	31	0.00750	−8288	18	0.00900	−8191	25
0.00400	−8493	34	0.006	−8347	78	0.00800	−8237	41	0.00950	−8167	21
0.00400	−8480	39	0.006	−8383	19	0.00800	−8270	18	0.01000	−8106	43
0.00600	−8394	23	0.0065	−8368	21	0.00800	−8222	20	0.01000	−8132	23
0.00550	−8424	30	0.007	−8295	61	0.00850	−8229	16	0.01000	−8146	16
0.00500	−8402	94	0.007	−8297	20	0.00900	−8153	45	0.01050	−8119	24
0.00500	−8470	28									
Cyclohexanone											
0.00350	−8260	71	0.00550	−8091	42	0.00700	−7922	40	0.00900	−7596	39
0.00400	−8192	50	0.00600	−7988	39	0.00750	−7777	31	0.00900	−7481^b	38
0.00400	−8305	64	0.00600	−8059	50	0.00800	−7804	34	0.00950	−7459^b	21
0.00450	−8148	29	0.00650	−7898	32	0.00800	−7767	36	0.01000	−7295^b	24
0.00500	−8072	37	0.00700	−7874	21	0.00850	−7653	34	0.01050	−7132^b	12
0.00500	−8203	68									
2,4-Pentanedione											
0.00400	1843	40	0.00600	2006	37	0.00700	2090	30	0.00900	2010^b	21
0.00400	1834	67	0.00600	1968	28	0.00800	2100	25	0.00900	2097^b	20
0.00400	1865	41	0.00600	1929	35	0.00800	2076	18	0.01000	1911^b	21
0.00500	1969	58	0.00700	2051	25	0.00800	2134	25	0.01000	1972^b	26
0.00500	1949	58	0.00700	2030	37	0.00900	2001^b	18	0.01000	1976^b	26
0.00500	1946	49									
Methyl Acetoacetate											
0.00400	−2241	33	0.00600	−2013	19	0.00700	−1917	15	0.00900	−1774	16
0.00400	−2223	29	0.00600	−2043	15	0.00800	−1850	14	0.00900	−1739	19
0.00400	−2190	30	0.00600	−2031	16	0.00800	−1822	17	0.01000	−1677	26
0.00500	−2146	22	0.00700	−1938	16	0.00800	−1857	16	0.01000	−1686	26
0.00500	−2129	23	0.00700	−1942	15	0.00900	−1764	14	0.01000	−1649	17
0.00500	−2103	25									
Ethyl Acetoacetate											
0.00400	−4594	57	0.00600	−4275	40	0.008	−3933	29	0.009	−3766	31
0.00400	−4660	67	0.00600	−4263	39	0.008	−3992	33	0.01	−3501	28
0.00500	−4468	53	0.00700	−4150	32	0.009	−3745	28	0.01	−3518	24
0.00500	−4515	45	0.007	−4072	42						

Table 2 (Continued)

2−Methoxyethyl Acetate											
0.00350	−11872	43	0.00550	−11589	34	0.00750	−11476	18	0.00950	−11184	17
0.00400	−11862	31	0.00600	−11657	22	0.00800	−11360	21	0.01000	−11128	15
0.00450	−11849	43	0.00650	−11575	29	0.00850	−11282	21	0.01050	−11072	13
0.00500	−11780	28	0.00700	−11541	20	0.00900	−11276	16			
2−Ethoxyethyl Acetate											
0.00350	−15335	98	0.00550	−14953	64	0.00700	−14653	54	0.00900	−14392	26
0.00400	−15325	48	0.00600	−14794	62	0.00750	−14638	45	0.00900	−14219	52
0.00450	−15143	68	0.00600	−14966	42	0.00800	−14565	39	0.00950	−14277	40
0.00500	−15249	135	0.00650	−14760	49	0.00800	−14434	55	0.01000	−14233	24
0.00500	−15009	65	0.00700	−14748	31	0.00843	−14483	30	0.01050	−14034	31
Methyl Methoxyacetate											
0.00285	−8831	136	0.00428	−8687	80	0.00571	−8605	58	0.00714	−8519	33
0.00285	−8802	104	0.00428	−8824	85	0.00571	−8669	42	0.00714	−8509	30
0.00300	−8843	98	0.00499	−8717	51	0.00600	−8679	48	0.00800	−8488	36
0.00356	−8824	68	0.00499	−8710	47	0.00642	−8538	30	0.00900	−8387	33
0.00356	−8675	62	0.00500	−8742	65	0.00700	−8590	35	0.01000	−8294	31
0.00400	−8798	72	0.00642	−8584	46						
Acetonitrile											
0.00400	−1343	21	0.00700	−1190	12	0.01000	−1044	8	0.02100	−520.8	7
0.00500	−1289	17	0.00800	−1147	11	0.01200	−948.0	8	0.02400	−390.3	6
0.00600	−1223	13	0.00900	−1093	9	0.01500	−805.6	8	0.02700	−252.6	8
0.00600	−1239	18	0.00900	−1081	10	0.01800	−663.6	6			
Propionitrile											
0.00400	−2992	88	0.00600	−2852	30	0.00900	−2594	53	0.01100	−2427	47
0.00400	−3029	45	0.00700	−2733	45	0.00900	−2617	19	0.01100	−2413	22
0.00500	−2908	63	0.00700	−2755	24	0.01000	−2505	49	0.01200	−2323	25
0.00500	−2941	32	0.00800	−2657	41	0.01000	−2511	22	0.01200	−2319	16
0.00600	−2817	58	0.00800	−2673	21						
Acrylonitrile											
0.00400	−2010	60	0.00700	−1762	24	0.00900	−1585	22	0.01100	−1396	17
0.00500	−1953	36	0.00800	−1676	23	0.01000	−1488	21	0.01200	−1298	18
0.00600	−1853	40	0.00800	−1679	23	0.01000	−1501	21	0.01200	−1293	19
0.00700	−1766	24	0.00900	−1593	23	0.01100	−1405	19			

[a] Standard deviation of signal fluctuations [b] Not included in the linear regression to obtain the value of $\bar{H}_1^{\mathrm{E},\infty}$.

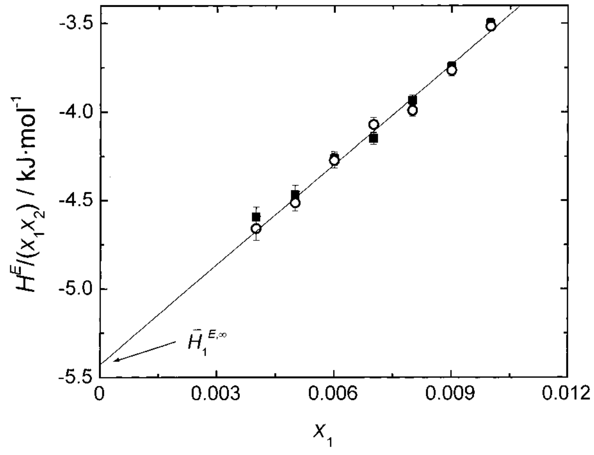

Figure 1. Example of measured excess enthalpy data and their extrapolation to infinite dilution. Ethyl acetoacetate(1) + water(2). (■) run 1; (○) run 2.

limit. The finding corresponds well with the 2% uncertainty in H^E/x_1x_2, which was estimated from error propagation combining all sources of error. A few deviations higher than 3% in Table 3 are observed typically in the case of older literature data and/or for acetonitrile exhibiting a quite small $\bar{H}_1^{\mathrm{E},\infty}$ effect. Note that the value for acetonitrile obtained in this work agrees very well with the highly accurate measurement of Stokes[15] and should be therefore considered superior to our previous result obtained with a Picker calorimeter.

Table 3. Experimental Limiting Partial Molar Excess Enthalpies $\bar{H}_1^{\mathrm{E},\infty}$ for 16 Organic Compounds in Water at 298.15 K, Parameter *B* in Equation 1, and Standard Deviation of Fit *s*

solute	$\bar{H}_1^{\mathrm{E},\infty}$ kJ·mol^{-1}	$s(\bar{H}_1^{\mathrm{E},\infty})$ [a] kJ·mol^{-1}	B kJ·mol^{-1}	$s(B)$[a] kJ·mol^{-1}	s[b]
1-butanol	−9.20	0.03	75.5	3.3	1.18
2-methyl-1-propanol	−9.18	0.05	62.0	6.4	1.42
cyclopentanol	−10.23	0.04	75.2	5.2	0.81
cyclohexanol	−8.46	0.05	77.2	17.0	0.55
2-butanone	−10.65	0.06	71.3	7.5	1.00
cyclopentanone	−8.74	0.02	60.4	1.8	0.69
cyclohexanone	−8.71	0.04	120.1	6.6	1.07
2,4-pentanedione	+1.62	0.04	59.9	5.8	0.92
methyl acetoacetate	−2.58	0.02	91.6	2.1	0.85
ethyl acetoacetate	−5.43	0.05	188.5	5.9	1.14
2-methoxyethyl acetate	−12.38	0.04	124.6	4.0	1.46
2-ethoxyethyl acetate	−15.98	0.06	179.7	7.2	1.41
methyl methoxyacetate	−9.07	0.03	76.3	4.8	0.88
acetonitrile	−1.51	0.01	46.9	0.3	0.72
propionitrile	−3.37	0.02	86.9	1.5	0.52
acrylonitrile	−2.42	0.01	92.8	1.0	0.36

[a] Standard deviation estimates resulting from fitting. [b] $s = [S_{\min}/(n-2)]^{1/2}$; $S_{\min} = \sum_{i=1}^{n}[(H^E/x_1x_2)_i^{\mathrm{exp}} - (H^E/x_1x_2)_i^{\mathrm{calc}}]^2/s^2(H^E/x_1x_2)_i^{\mathrm{exp}}$.

Except for 2,4-pentanedione, the limiting partial molar excess enthalpies are for all compounds negative, indicating that the process of their dissolution in water is energetically favored at room temperature. A striking difference in the values of $\bar{H}_1^{\mathrm{E},\infty}$ for 2-butanone and 2,4-pentadione is probably a consequence of the tautomerism of the latter compound that is caused in turn by the strong intramolecular interaction of two β-position keto groups in the

Table 4. Comparison of Limiting Partial Molar Excess Enthalpies $\bar{H}_1^{E,\infty}$ at 298.15 K Obtained in This Work with Experimental Values from the Literature and with Estimates by Two Group Contribution Methods

solute	$\bar{H}_1^{E,\infty}$ this work kJ·mol^{-1}	$\bar{H}_1^{E,\infty}$ literature kJ·mol^{-1}	ref	diff[a] %	$\bar{H}_1^{E,\infty}$ UNIFAC[b] kJ·mol^{-1}	$\bar{H}_1^{E,\infty}$ Cabani et al.[c] kJ·mol^{-1}
1-butanol	−9.20	−9.37[d]	16	+1.9	−1.58	−9.94
		−8.74[d]	17	−5.0		
		−9.32[d]	18	+1.3		
		−9.32[d]	19	+1.3		
		−9.24	20	+0.4		
		−9.42	21	+2.4		
		−9.21	22	+0.1		
		−9.00	23	−2.2		
		−9.28	24	+0.9		
		−9.04	25	−1.7		
2-methyl-1-propanol	−9.18	−9.22	20	+0.5	−1.58	−10.53
		−9.32	21	+1.5		
cyclopentanol	−10.23	−10.13	26	−1.0	+2.59	−10.71
		−10.35	21	+1.2		
cyclohexanol	−8.46	−8.72	27	−6.5	+4.86	−8.82
		−7.91	26	+3.1		
		−9.02	21	+6.6		
2-butanone	−10.65	−10.72	28	+0.7	−2.35	−10.29
		−10.82	1	+1.6		
cyclopentanone	−8.74	−8.96	1	+2.6	+1.48	−8.51
cyclohexanone	−8.71	−8.73	1	+0.2	+3.36	−9.24
2,4-pentanedione	+1.62				−6.17	−26.45[e]
methyl acetoacetate	−2.58				−6.66	[f]
ethyl acetoacetate	−5.43				−6.51	[f]
2-methoxyethyl acetate	−12.38				−4.50	−19.51[e]
2-ethoxyethyl acetate	−15.98				−3.72	−20.33[e]
methyl methoxyacetate	−9.07				−4.08	[f]
acetonitrile	−1.51	−1.61[d]	14	+6.6	−0.10	−2.63
		−1.49[d]	17	−1.3		
		−1.54	15	+1.7		
		−1.56	29	+3.3		
		−1.75	1	+15.9		
propionitrile	−3.37	−3.29[d]	17	−2.4	−0.05	−2.78
		−3.65	1	+8.3		
acrylonitrile	−2.42				+5.47	[f]

[a] diff = $(\bar{H}_{1,\mathrm{lit}}^{E,\infty} - \bar{H}_{1,\mathrm{exp}}^{E,\infty})/\bar{H}_{1,\mathrm{exp}}^{E,\infty} \times 100\%$. [b] Modified UNIFAC (Dortmund).[2–5] [c] Group contribution method of Cabani et al.[1] gives enthalpy of hydration; enthalpy of vaporization needed to calculate $\bar{H}_1^{E,\infty}$ was taken from CDATA[30] or Riddick et al.[31] [d] Flow mixing calorimetry. [e] Based on parameters for monofunctional solutes; corrections for intramolecular influencing of characteristic groups not available. [f] Enthalpy of vaporization not available.

bifunctional molecule. Consistently, acetoacetates containing also β-position carbonyl groups exhibit much less negative values of $\bar{H}_1^{E,\infty}$ than do similar alkoxyacetates.

Two group contribution methods, namely, that of Cabani et al.[1] and the modified UNIFAC (Dortmund)[2–5], were tested to predict the limiting partial molar excess enthalpies for the solutes studied. The method of Cabani et al. is designed to predict the enthalpy of hydration, so to obtain $\bar{H}_1^{E,\infty}$, data on the enthalpy of vaporization are needed. Neither is the modified UNIFAC method directly focused on prediction of $\bar{H}_1^{E,\infty}$ because its parameters are not based on $\bar{H}_1^{E,\infty}$ data. As seen from Table 4, the method of Cabani et al. gave fairly good results for monofunctional derivatives, but failed for the bifunctional ones, the failure being obviously caused by missing correction parameters for intramolecular interaction of the characteristic groups. The modified UNIFAC (Dortmund) yielded completely unsatisfactory results.

Acknowledgment

We thank Dr. V. Hynek for his precious help with construction of electronic equipment and M. Barošová for performing preliminary test experiments.

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Received for review January 14, 2002. Accepted April 20, 2002. Š.H. is grateful for financial support from the Program International de Coopération Scientifique (CNRS PICS 262) and for hospitality of its coordinator, Dr. V. Majer. This work was further supported by a MSM 2234 00008 grant from the Ministry of Education of the Czech Republic and a NATO Environmental and Earth Science and Technology Collaborative Linkage Grant EST.CLG.978291.

JE020002U