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Group Contributions for an Estimation of Partial Molar Volumes at Infinite Dilution for Aqueous Organic Solutes at Extended Ranges of Temperature and Pressure[1]

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Experimental data on the partial molar volume at infinite dilution in water for two groups of organic solutes (derivatives of benzene and aliphatic hydroxyl derivatives) measured using a vibrating-tube densimeter in the temperature and pressure ranges 298 to 573 K and 0.1 to 30 MPa are summarized. Smoothed values of partial molar volume as a function of temperature and pressure are employed for the evaluation of group and structural contributions. The contributions are used to estimate the partial molar volumes at infinite dilution in water for various solutes. The average deviation between partial molar volumes calculated from the contributions and the experimental data employed for the evaluation of the contributions is less than 1 $\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ in most cases. Predictions of partial molar volumes of solutes not included in the evaluation of the contributions are performed and results are compared with experimental data.

KEY WORDS: aqueous solutions; group contribution; infinite dilution; partial molar volume.

1. INTRODUCTION

The partial molar volume at infinite dilution in water (standard partial molar volume) is a property that is essential in a process to obtain the solute standard chemical potential in wide ranges of temperature and pressure. A systematic study of selected organic solutes is in progress in our

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laboratory. A large set of experimental data is already available, and thus a development of a group contribution method for estimation of partial molar volumes is possible. Estimation methods for partial molar volumes published in the literature (e.g., recent paper by Lepori and Gianni [1]) are limited mostly to the temperature 298.15 K and atmospheric pressure. Here we present an attempt to develop a simple group contribution method for estimation of standard partial molar volumes in extended ranges of temperature.

2. EXPERIMENTAL DATA

In the course of several years partial molar volumes at infinite dilution in water of solutes of the aromatic series (benzene and its mono- and disubstituted derivatives) have been systematically studied in our laboratory. A vibrating-tube densimeter [2] designed for measurements in the temperature range 298 to 573 K and at pressures up to 30 MPa was used for measurements. Data for phenol [2], cresols [3], dihydroxybenzenes [4], aniline [5], benzoic acid and its hydroxyderivatives [6] and aminoderivatives [9], toluidines [7], chlorophenols [8], *o*-phenylendiamine [9], nitrobenzene and nitrophenols [10], and *m*-aminophenol, benzonitrile, and *o*-cyanophenol [11] have been already published. This study has been completed by measurements of aqueous benzene and toluene [12]. Recently a systematic investigation of some phenyl derivatives of aliphatic solutes (as intermediate solutes between aromatic and aliphatic series) and aliphatic solutes (mono- and polyhydric alcohols) [13] has been launched. In the present study data for phenylmethanol and 1-alkanols from methanol to 1-butanol are included. A list of solutes is presented in Table I along with temperature ranges of experimental data. Data for several solutes do not cover the entire temperature range due to decomposition at higher temperatures.

The above mentioned experimental data [2–13] for 35 organic solutes were obtained for particular pairs of temperature and pressure. An empirical function of temperature and pressure was employed to smooth the data for each solute. Values of partial molar volume along the saturation curve of water (i.e., at the saturated vapor pressure of water) were calculated from the function and used to evaluate group contributions. Therefore, only one variable (temperature) is assumed below.

3. GROUP CONTRIBUTION METHOD

The design of a group contribution method depends on both the molecular structures to be described and the amount of available data.

Table I. Ranges of Deviations, Root-Mean Square Deviations (RMSD), and Biases (Average Deviations) of Values of Partial Molar Volume Calculated Using Group and Structural Contributions from Experimental Data. (T_{max} is the Highest Temperature of Experimental Data; the Lowest Experimental Temperature is 298 K for all Solutes.)

Solute	Deviations from	to	RMSD	Bias	T_{max}	Solute	Deviations from	to	RMSD	Bias	T_{max}
	($cm^3 \cdot mol^{-1}$)				(K)		($cm^3 \cdot mol^{-1}$)				(K)
benzene	−2.20	0.23	0.45	−0.29	573	2-hydroxybenzoic acid	−1.30	1.90	0.89	−0.36	443
methylbenzene	−2.50	1.40	1.09	−0.70	573	3-hydroxybenzoic acid	−0.80	5.30	1.39	0.13	498
hydroxybenzene	−1.10	−0.27	0.28	−0.65	573	4-hydroxybenzoic acid	−3.20	0.57	0.74	−0.37	498
aminobenzene	−1.20	0.38	0.41	−0.63	573	1-hydroxy-2-chlorobenzene	−0.46	0.60	0.27	0.30	573
benzoic acid	−0.07	3.70	0.91	0.45	473	1-hydroxy-4-chlorobenzene	−0.72	1.60	0.56	−0.13	573
chlorobenzene	−0.98	0.97	0.51	−0.17	573	1-hydroxy-2-nitrobenzene	−1.60	0.14	0.36	−0.11	523
nitrobenzene	−1.20	1.80	0.97	0.42	573	1-hydroxy-3-nitrobenzene	−1.50	0.26	0.50	−0.50	573
cyanobenzene	−0.13	0.30	0.14	0.09	573	1-hydroxy-4-nitrobenzene	−0.56	0.88	0.42	0.19	548
1-hydroxy-2-methylbenzene	−0.53	1.40	0.29	0.08	573	1-hydroxy-2-cyanobenzene	−0.38	0.70	0.27	−0.11	498
1-hydroxy-3-methylbenzene	−1.20	0.29	0.30	−0.14	573	2-aminobenzoic acid	−0.56	1.10	0.60	0.30	498
1-hydroxy-4-methylbenzene	−0.71	0.54	0.30	0.02	573	3-aminobenzoic acid	−2.10	0.96	0.96	−0.17	498
1,2-dihydroxybenzene	−2.20	0.54	0.63	−0.03	498	1,2-diaminobenzene	−0.59	0.51	0.34	0.00	573
1,3-dihydroxybenzene	−0.57	−0.10	0.12	−0.30	498	phenylmethanol	0.18	4.50	1.11	1.90	573
1,4-dihydroxybenzene	−0.44	0.27	0.16	0.10	498	methanol	0.36	2.20	0.51	0.86	573
1-amino-3-hydroxybenzene	−1.30	0.34	0.44	−0.21	573	ethanol	−0.61	−0.02	0.15	−0.18	573
1-amino-2-methylbenzene	−0.26	0.30	0.12	−0.08	573	1-propanol	−1.20	−0.01	0.31	−0.29	573
1-amino-3-methylbenzene	0.03	1.70	0.38	0.47	573	1-butanol	−0.60	0.13	0.21	−0.38	573
1-amino-4-methylbenzene	−0.16	0.83	0.36	0.34	573						

Generally, data for more compounds allow more detailed set of groups and *vice versa*. With respect to available data, the following groups are defined:

C_6H_4 (aromatic ring with four hydrogen atoms); –H; $-CH_3$; $-CH_2-$, –OH; $-NH_2$; $-NO_2$; –Cl; –COOH; –CN. Contributions of substituent groups are assumed to be the same when bonded to the aromatic ring and in aliphatic derivatives. Our data for di-substituted aromatic derivatives show, however, that while 1,3- and 1,4- (*m*- and *p*-) isomers have nearly identical values of partial molar volumes (mostly within the experimental uncertainty), partial molar volumes of 1,2- (*o*-) isomers differ from those of 1,3- and 1,4-isomers. Therefore a structural contribution is introduced for each substituent group (except for hydrogen) for 1,2- isomers, i.e., a total of seven structural contributions: *o*-CH_3, *o*-OH, *o*-NH_2, *o*-NO_2, *o*-Cl, *o*-COOH, and *o*-CN. The partial molar volume is expressed as

$$V^0 = \sum_i N_i(G_i + S_i) \tag{1}$$

where N_i is the number of groups of type i in a molecule, G_i is the volume of the group (group contribution), and S_i is the volume of structural contribution. For example, the partial molar volume of *o*-cresol (1-hydroxy-2-methylbenzene) is expressed as $G(C_6H_4) + \{G(CH_3) + S(o\text{-}CH_3)\} + \{G(OH) + S(o\text{-}OH)\}$ while those of *m*- and *p*-cresol are $G(C_6H_4) + G(CH_3) + G(OH)$. Non-branched aliphatic chains are constructed from $-CH_3$ and $-CH_2-$ groups and, therefore, the group contribution of the hydrogen atom, $G(H)$, is related only to hydrogen bonded to the aromatic ring.

Values of group and structural contributions were evaluated using the weighted least-squares method. The objective function was defined as

$$\Phi(G, S) = \sum_k w_k(V^0_{k,\mathrm{exp}} - V^0_{k,\mathrm{calc}})^2, \qquad G = \{G_i\}, \quad S = \{S_i\} \tag{2}$$

where $V^0_{k,\mathrm{exp}}$ is the experimental value of the partial molar volume of the kth solute and $V^0_{k,\mathrm{calc}}$ is its value calculated from Eq. (1). Statistical weights w_k were derived from estimated experimental uncertainties $\delta V^0_{\mathrm{exp}}$ as $w_k = 1/(\delta V^0_{k,\mathrm{exp}})^2$. Uncertainties of resulting values of group and structural contributions were estimated from a covariance matrix.

4. RESULTS

4.1. Group and Structural Contributions

Calculations with the entire set of above defined contributions revealed that structural contributions $S(o\text{-}Cl)$ and $S(o\text{-}CN)$ are zero within the estimated uncertainty in the whole temperature range. The results of the consequent evaluation of ten group contributions and remaining five structural contributions ($S(o\text{-Cl})=S(o\text{-CN})=0$) for temperatures in the range 273 to 573 K are shown in Fig. 1. Group contributions increase with increasing temperature except for the contributions of two hydrophilic groups (–OH and $-NH_2$). Structural contributions are small and moderately dependent on temperature except for *o*-COOH. Temperature ranges for –COOH, *o*-COOH, and *o*-NO_2 contributions are limited to a maximum temperature of about 500 K since the respective solutes decomposed at higher temperatures and data are not available. The temperature dependences of group contributions were expressed as the polynomial function,

$$G \text{ or } S/(\text{cm}^3\cdot\text{mol}^{-1}) = \sum_{i=0}^{4} A_i (T/\text{K})^i, \tag{3}$$

and the values of parameters A_i are given in Table II.

Deviations of partial molar volumes calculated using group and structural contributions from experimental values are presented in Table I for solutes, the data of which were used for the evaluation of contributions. The highest positive deviation is $5.3\ \text{cm}^3\cdot\text{mol}^{-1}$ (3-hydroxybenzoic acid at 498 K), and the highest negative deviation is $-3.2\ \text{cm}^3\cdot\text{mol}^{-1}$ (4-hydroxybenzoic acid at 498 K). These extreme deviations are observed at the upper limit of the experimental temperature range. This indicates that the decomposition of the solutes might occur even at this temperature. The lowest value of RMSD ($0.12\ \text{cm}^3\cdot\text{mol}^{-1}$) is observed for 1,3-dihydroxybenzene and 1-amino-2-methylbenzene, and the highest RMSD ($1.39\ \text{cm}^3\cdot\text{mol}^{-1}$) for 3-hydroxybenzoic acid. The average RSMD deviation over all 35 solutes is $0.50\ \text{cm}^3\cdot\text{mol}^{-1}$.

4.2. Prediction of Partial Molar Volumes

The predictive ability of the method was examined by a comparison of partial molar volumes calculated for solutes not included in the data set employed for evaluation of contributions with selected experimental data. Experimental data used for a comparison were mostly taken from papers that present data compilations [1, 14, 15] and from a few other papers [16–18]. Some data were obtained recently in our laboratory (2-phenylethanol, phenylethanoic acid, 1,2,3-trihydroxybenzene, 1,4-dihydroxy-2-methylbenzene, 1,2-benzenedicarboxylic acid, and 1,2,4-benzenetricarboxylic acid). These data were not included in the evaluation of contributions. The measurements for 2-phenylethanol are in progress and will be included in future modifications of the method along with data for an

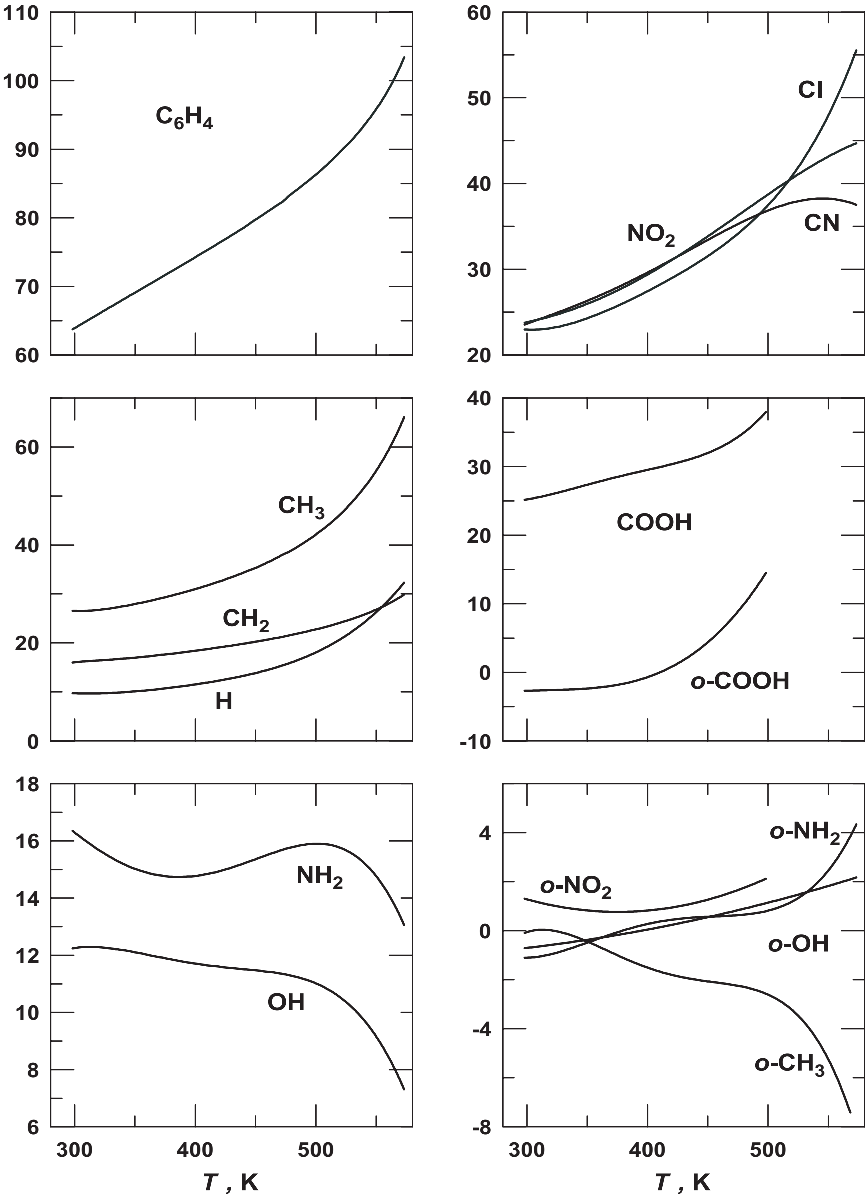

Fig. 1. Dependences of group and structural contributions on temperature. The scales of vertical axes are in $cm^3 \cdot mol^{-1}$.

Table II. Parameters of Eq. (3)

Group	A_0	A_1	$A_2 \cdot 10^2$	$A_3 \cdot 10^5$	$A_4 \cdot 10^8$	T_{max} (K)
C_6H_4	228.075	−1.94181	0.79952	−1.38344	0.89524	573.15
H	180.520	−1.75850	0.67425	−1.15280	0.75540	573.15
CH_3	463.406	−4.47170	1.69147	−2.82106	1.77934	573.15
CH_2	113.080	−1.00488	0.38053	−0.63017	0.39759	573.15
Cl	333.110	−3.14670	1.17510	−1.93120	1.20640	573.15
NO_2	9.094	0.22063	−0.12826	0.30441	−0.22486	573.15
CN	−71.987	0.99836	−0.41062	0.77074	−0.52356	573.15
COOH	408.910	−4.31880	1.78710	−3.23390	2.18150	498.15
NH_2	−36.366	0.75353	−0.35920	0.69955	−0.48149	573.15
OH	−114.400	1.31390	−0.50321	0.84466	−0.52694	573.15
o-CH_3	−286.370	2.92840	−1.10220	1.81150	−1.10290	573.15
o-NO_2	13.469	−0.06763	0.00900			498.15
o-COOH	−93.924	0.85219	−0.26642	0.27908		498.15
o-NH_2	161.800	−1.71520	0.66146	−1.10770	0.68419	573.15
o-OH	−0.831	−0.00484	0.00176			573.15

extended set of aliphatic solutes. The data for other solutes cover narrow temperature ranges since the decomposition was observed at temperatures higher than 373 K (1,4-dihydroxy-2-methylbenzene was measured at 298 K only due to its instability even at ambient temperature).

Predicted partial molar volumes are compared in Table III with values taken from the literature. Agreement observed for benzene derivatives is quite satisfactory except for solutes with the carboxyl group. A probable reason can be seen in the fact that no data for a solute with two carboxyl groups in 1,2-position were included in the data set employed for evaluation group and structural contributions. The effect of intramolecular interaction of two large –COOH groups would probably lead to a different structural contribution *S*(*o*-COOH). Despite the fact that the group contribution *G*(COOH) was evaluated for aromatic solutes only, it gives reasonable predictions for aliphatic carboxylic acids, at least at lower temperatures (see Table III). Estimates for higher members of 1-alkanol series and for polyhydric aliphatic derivatives are mostly in satisfactory agreement with experimental values at 298 K except for 1,2,3-propanetriol. Here the vicinity of three hydroxyl groups probably plays a role.

Tentative predictions were made for several other aliphatic solutes (amino derivatives, acetonitrile, chloromethane). The estimates are systematically higher than experimental data. No data for aliphatic solutes with the groups –NH_2, –CN, and –Cl were included in the evaluation of the contribution, and thus the disagreement is not surprising. Future modifications of the method would definitely include introduction of separate

Table III. Comparison of Partial Molar Volumes Calculated from Group and Structural Contributions, $(V^0)_{calc}$, with Literature Data, $(V^0)_{lit}$. (Estimated Uncertainties $s((V^0)_{calc})$ were Calculated from Uncertainties of Contributions.)

	T	$(V^0)_{calc}$	$s((V^0)_{calc})$	$(V^0)_{lit}$	calc-lit
	(K)	$(cm^3 \cdot mol^{-1})$			
ethylbenzene	298	116.07	0.80	114.50	1.57
propylbenzene	298	132.07	0.89	131.00	1.07
2-phenylethanol	298	117.74	0.89	117.36	0.38
	408	136.00	0.89	133.90	2.10
phenylethanoic acid	298	114.66	0.80	114.61	0.05
	408	135.50	0.80	132.80	2.70
1,2,3-trihydroxybenzene	298	87.87	1.20	87.95	−0.09
	408	98.75	1.20	98.21	0.54
1,3,5-trihydroxybenzene	298	90.71	0.89	92.10	−1.39
1,4-dihydroxy-2-methylbenzene	298	104.23	1.06	104.65	−0.42
1,2-benzendicarboxylic acid	298	108.65	0.89	114.91	−6.26
	408	134.50	0.89	131.70	2.80
2,6-dimethylbenzoic acid	298	126.69	1.20	132.60	−5.91
1,2,4-benzenetricarboxylic acid	298	124.05	1.06	129.02	−4.97
	373	142.30	1.06	143.30	−1.00
methane	298	36.32	0.57	37.30	−0.98
	573	98.33	0.86	106.00	−7.67
ethane	298	53.13	0.57	52.90	0.23
propane	298	69.13	0.69	67.00	2.13
1-pentanol	298	102.80	0.98	102.40	0.40
1-hexanol	298	118.80	1.06	117.56	1.24
1-heptanol	298	134.80	1.13	133.40	1.40
1,2-ethanediol	298	56.48	0.80	54.60	1.88
1,2-propanediol	298	72.48	0.89	71.22	1.26
1,3-propanediol	298	72.48	0.89	71.89	0.59
1,2,3-propanetriol	298	74.16	1.06	70.95	3.21
1,4-butanediol	298	88.48	0.98	88.35	0.13
1,5-pentanediol	298	104.50	1.20	104.30	0.20
	521	142.06	1.20	138.20	3.86
ammonia	298	26.11	0.57	24.85	1.26
	573	45.35	0.86	49.60	−4.25
hydrazine	298	32.70	0.57	30.13	2.57
1,2-diaminoethane	298	64.70	0.80	62.88	1.82
1,3-diaminopropane	298	80.70	0.89	78.83	1.87
1,4-diaminobutane	298	96.70	0.98	93.60	3.10
methanoic acid	298	34.92	0.57	34.70	0.21
ethanoic acid	298	51.72	0.57	51.90	−0.18
	373	57.63	0.47	57.26	0.37
	473	72.20	0.92	67.69	4.51
propanoic acid	298	67.72	0.69	67.90	−0.18
	373	75.22	0.57	74.99	0.23
	473	93.48	1.13	89.41	4.07
butanoic acid	298	83.72	0.80	84.60	−0.88
pentanoic acid	298	115.71	0.98	116.00	−0.29
acetonitrile	298	50.13	0.57	47.40	2.73
chloromethane	298	49.56	0.57	46.20	3.36

group contributions for groups bonded to the benzene ring and to aliphatic chains. The need for new experimental data is obvious.

5. CONCLUSION

The results show that the proposed simple additivity scheme yields reasonable results even in a wide range of temperature from ambient up to 573 K. Despite the fact that aromatic solutes were limited to mono- and di-substituted benzene derivatives, the prediction of partial molar volumes of tri-substituted benzene derivatives is satisfactory. Few solutes of aliphatic series were included in this study. Future measurements will extend the experimental data set, and, therefore, a reformulation of the group contribution method will be possible which may improve its descriptive and predictive capabilities.

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