



Conformational analysis of branched alkanes using limiting partial molar volumes



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ABSTRACT

The solvent effect on the solute conformations of straight and branched-chain alkanes infinitely diluted in methanol and carbon tetrachloride is studied. An additive scheme is used that takes into account the strong relation between limiting partial molar volumes and the average numbers of gauche conformations adopted by the solute molecules in each solvent. These numbers were determined using the Pitzer's steric partition function with different values of anti→gauche transition enthalpy variations, ranging from (+2931 to −1465) kJ·mol^{−1}. The partial molar volumes at infinite dilution for three mono branched-chain alkanes (2-methylpentane, 3-methylpentane and 2-methylheptane) were experimentally determined in methanol to complement other series consisting mainly of straight, bi and tri branched-chain alkanes obtained in previous works. The conformational analysis performed using statistical methods is quite convincing about the strong effect of the solvent on the solute conformation equilibrium. Conclusions about close-packing and structure effects related to anti-gauche transitions in these two solvents are also drawn.

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1. Introduction

Conformational analysis has been frequently used in several chemistry domains in order to rationalize the behaviour of flexible molecules in terms of molecular interactions in liquid solutions and mixtures as well as at several types of interfaces. The very different conformational behaviour that a given flexible molecule presents in the gas phase and in pure liquids when compared to liquid mixtures where it can act both as a solute or solvent makes this subject so important. Reasoning to explain the folding or unfolding of proteins, the mechanisms of many kinds of reactions and catalytic effects in homogeneous or heterogeneous media are often based on conformational analysis [1–3].

Spectroscopic techniques and in particular Raman spectroscopy [4–6] have been widely used to assess the most probable molecular conformations and in some cases their relative abundance. Computational studies have also proliferated in literature [7–9].

It has been proved that the conformational distribution of a given flexible solute in a solvent, described by the average number of gauche interactions, Z_g , has a decisive influence on thermophysical properties of the solute in its own medium or of the solute infinitely diluted in a solvent [10–14]. Some qualitative reasoning, based on Z_g changes with composition, have also been made to justify some interesting features found in the very-dilute region of aqueous mixtures of amphiphilic molecules with a flexible hydrophobic moiety [15–18].

Several additive schemes [19–24] based on group contributions, or using reference volumes such as van der Waals volumes calculated according to Bondi [25], have been proposed to calculate limiting partial molar volumes, at a fixed temperature and pressure. Some of them include a term containing the average number of gauche interactions, Z_g , in order to take into account experimental values obtained for different isomeric solutes. As far as we know, the solvent effect on Z_g values concerning 1–4 carbon–carbon interactions has not yet been considered. This is however imperative, given that the volume changes produced by each gauche interaction depend on the cohesive energy density (c.e.d.) of that solvent and can be represented by the enthalpy change for the anti→gauche (a→g) conversion, $\Delta H(a\rightarrow g)$ [26]. Apparently, calculations of Z_g values have been made considering always the same $\Delta H(a\rightarrow g) = 2931$ kJ·mol^{−1} value. Examples are calculations for series of straight and branched-chain alkanes, using the Pitzer's steric partition function [27], made by Edward et al. (in carbon tetrachloride) [12] and Criss et al. (in methanol) [13]. Also, the same $\Delta H(a\rightarrow g)$ value was used by Mann [10,11] in pure alkanes.

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In this work we measured partial molar volumes at infinite dilution, V_B^∞ , for three mono branched-chain alkanes, 2-methylpentane (2M-5), 3-methylpentane (3M-5) and 2-methylheptane (2M-7), in methanol with the aim of using limiting partial molar volumes as a quantitative tool to provide a clear confirmation that the conformational equilibrium of flexible molecules at infinite dilution strongly depends on the solvent used. These compounds were chosen in order to complement series of branched and straight-chain alkanes, published by French and Criss [13] and by Barbosa et al. [28]. Values of the average number of 1–4 carbon–carbon gauche interactions were calculated using the Pitzer steric partition function [27] with $\Delta H(a \rightarrow g)$ varying from +2931 to $-1465 \text{ kJ}\cdot\text{mol}^{-1}$. Resorting to the same additive scheme as used by Edward et al. [12], French and Criss [13] and Inglese et al. [14] and applying a multi-parametric least-squares fitting to the whole set of straight and branched-chain alkanes we prove that other values than +2931 $\text{kJ}\cdot\text{mol}^{-1}$ should be considered in order to grasp the best $a \rightarrow g$ equilibrium. We further made the same type of analysis based on 20 straight and branched-chain alkanes in carbon tetrachloride, CCl_4 , to confirm that in this solvent the best least-squares fitting is obtained with $\Delta H(a \rightarrow g) = +2931 \text{ kJ}\cdot\text{mol}^{-1}$, as used by Edward et al. following Mann's proposal for pure compounds.

In order to shed light into the meaning of the obtained $\Delta H(a \rightarrow g)$ values for the two solvents, we used a simple continuum model to get an independent estimate of these quantities taking into account several contributions.

2. Experimental

2.1. Materials

Methanol *p.a.* was supplied by Merck, with purity quoted >0.998 in mass fraction. It was further purified as previously described [28,29]. Its purity was tested by density measurements. The 2-methylpentane and 3-methylpentane were furnished by Fluka with purity claimed >0.995. 2-methylheptane with purity quoted >0.99 in mass fraction was supplied by Merck. The three mono branched-chain alkanes were used without further purification. Table 1 summarizes this information. All the density values

Table 2

Densities, $\rho/\text{kg}\cdot\text{m}^{-3}$, of pure 2-methylheptane (2M-7), 2-methylpentane (2M-5), 3-methylpentane (3M-5), methanol, toluene and *n*-heptane at $T = 298.15 \text{ K}^a$ and $P = 0.1 \text{ MPa}^a$.

Compounds	$\rho/\text{kg}\cdot\text{m}^{-3}$	Ref.
2-Methylheptane (2M-7) ^b	693.9 ^c	This work
	698.2	[31]
	698.0	[32]
	687.9	[33]
	691.7	[34]
2-Methylpentane (2M-5) ^b	648.48 ^d	This work
	648.52	[35]
	648.47	[36]
	648.63	[37]
3-Methylpentane (3M-5) ^b	659.76 ^d	This work
	659.76	[35]
	659.73	[37]
	659.79	[36]
Methanol	786.57 ^e	This work
	786.60	[38]
	0.78663	
	786.63	[39]
	786.58	[28]
Toluene	786.55	[40]
	862.21 ^f	This work
	862.2	[41,42]
	862.24	[43]
	862.1	[44]
<i>n</i> -Heptane	679.46 ^d	This work
	679.47	[43]
	679.49	[45]
	679.68	[46]
	679.58	[47]
	679.48	[48]
	679.44	[33]
679.49	[49]	

^a Standard uncertainties $u(T) = 0.01 \text{ K}$ and $u(P) = 0.002 \text{ MPa}$.

^b The notation used for branched-chain alkanes is the same as used by Mann et al. [10].

^c $u_{c,r}(\rho) = 0.001$.

^d $u_{c,r}(\rho) = 0.0005$.

^e Value obtained after averaging all density measurements made during the determination of apparent molar volumes in the three solutes studied. $u_{c,r}(\rho) = 0.0002$.

^f $u_{c,r}(\rho) = 0.00005$.

Table 1

Name, molar mass, CAS number, chemical formula, source, purity and purification method.

Compounds under study	Methanol	2-Methylheptane	2-Methylpentane	3-Methylpentane
Molar Mass/ $\text{kg}\cdot\text{mol}^{-1}$	0.0320419	0.1142285	0.0861754	0.0861754
Chemical Formula	CH_3OH	C_8H_{18}	C_6H_{14}	C_6H_{14}
CAS number	65-56-1	592-27-8	107-83-5	96-14-0
Source	Merck	Merck	Fluka	Fluka
Purity/mass fraction	>0.998 As stated by the supplier	>0.99 As stated by the supplier	>0.995 As stated by the supplier	>0.995 As stated by the supplier
Purification method	Fractionally distilled under dry N_2 ^a	Used as received	Used as received	Used as received
Calibrants	Water	Heptane	Toluene	
Molar Mass/ $\text{kg}\cdot\text{mol}^{-1}$	0.01801528	0.1002019	0.0921384	
Chemical Formula	H_2O	C_7H_{16}	C_7H_8	
CAS number	7732-18-5	142-82-5	108-88-3	
Source	Deionized	Fluka <i>p.a.</i>	B.D.H. AristarR	
Purity	High purity water of grade 1 (ISO3696:1995E) ^b	>0.995 ^c in mass fraction as stated by the supplier	>0.9995 in mass fraction as stated by the supplier	
Purification method	Redistilled over KMnO_4 under dry N_2	Used as received	Used as received	

^a Ref. [29].

^b From Milli-Q system supplied by Millipore, resistivity: $18 \times 10^4 \Omega\cdot\text{m}$.

^c Máx. isomers 0.005 in mass fraction.

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