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Partial Molar Volumes of Severely Hindered β-Diketones with α-Adamantyl Groups

M. F. Rey-Stolle,[†] C. Salom,[‡] J. Marquet,[§] M. Moreno-Mañas,[§] and I. Hernández-Fuentes*,[†]

Departamento de Química Física I, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain, ETSI Aeronáuticos, Universidad Politécnica, 28040 Madrid, Spain, and Departamento de Química, Universitat Autònoma de Barcelona, Bellaterra, 08193 Barcelona, Spain

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Partial molar volumes of several α-adamantyl β-diketones and adamantane were determined by density measurements. The effect of solvent and structure of the α-substituents and the size of the end groups were analyzed. Good agreement was observed between the experimental molar volumes and the values calculated by group contributions; in all the cases the differences were less than 4%.

Introduction

α-Substituted β-diketones are compounds of great interest because the equilibrium between the keto and enol tautomers depends, to a great extent, on the nature of the α-substituents. This equilibrium is completely shifted to the keto form when, at least, one of the β-diketone substituents is big enough (*1*, *2*).

To the best of our knowledge, only partial molar volumes of β-diketones in which mixtures of both the keto and enol tautomers exist have been measured (*3*, *4*).

The aim of this work is to determine the limiting partial molar volume at infinite dilution, V_2^∞, of several β-diketones bearing bulky substituents at the intercarbonyl positions, namely, four α-adamantyl β-diketones in which only the keto form is present (*2*).

The structures of the selected compounds are shown in Figure 1. Compounds 1AdDKMe, 1AdDKBu^t, and 1AdMeDKMe have the adamantyl group attached by its 1-position, and compound 2AdDKMe has the adamantyl group by its 2-position.

Compounds 1AdDKMe and 2AdDKMe allow the influence of the position by which the adamantyl group is attached to the β-diketone on the value of the molar volume to be studied.

The solvent effect is analyzed in β-diketones 1AdDKMe and 1AdDKBu^t. In these two compounds, the molar volumes are also compared to study how the substitution of the end methyl groups by *tert*-butyl groups affects the value of the studied magnitude.

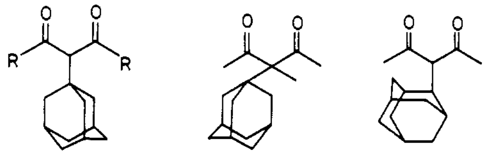
The influence of the substitution of the hydrogen atom for a methyl group at the intercarbonyl position in compound 1AdMeDKMe on V_2^∞ is also discussed.

Besides, the partial molar volume of adamantane is determined in cyclohexane solution at 298.15 K in order to compare this value with the previously obtained ones in several solvents (*5*, *6*).

Finally, the experimental partial molar volumes of all the compounds before mentioned are compared with the ones calculated by group contributions (*7*).

Experimental Section

Materials. Adamantane ($C_{10}H_{16}$, tricyclo[3.3.1.1^{3,7}]decane, Aldrich Chemie, 99+%) was used without purification. The α-adamantyl β-diketones 3-(1-adamantyl)pentane-2,4-dione (1AdDKMe), 4-(1-adamantyl)2,2,6,6-tetramethylheptane-3,5-dione (1AdDKBu^t), 3-(1-adamantyl)-3-methylpentane-2,4-dione (1AdMeDKMe), and 3-(2-adamantyl)pentane-2,4-dione (2AdDKMe) were synthesized as indicated in ref 2. The purity of all the β-diketones was confirmed by correct elemental analysis (*2*) for C and H within ±0.4.



1AdDKMe : R=Me
1AdDKBu^t : R=Bu^t
1AdMeDKMe
2AdDKMe

Figure 1.

Cyclohexane and benzene (Carlo Erba of RPE quality, 99.5+%), were dried over Merck 4-Å molecular sieves.

Densimetry. Densities were measured with a vibrating tube digital densimeter (Anton Paar DMA 55) with a maximum error of ±1 × 10^{-5} g/cm^3. Distilled water and air were used as calibrating substances. The temperature in the measuring cell was regulated to 298.15 ± 0.01 K. The solutions for density measurements were prepared by mass. The error in the composition expressed by mass fraction was, in all cases, less than ±2.5 × 10^{-7}.

Partial Molar Volume. The partial molar volume at zero concentration, V_2^∞, has been determined by extrapolation to infinite dilution of the apparent molar volume of the solute, V^{app}, calculated as

$$V_2^{app} = M_2\left[\rho_1^{-1} + \frac{\rho^{-1} - \rho_1^{-1}}{w_2}\right] \qquad (1)$$

where M_2 is the molecular weight of the solute, ρ_1 and ρ are the densities of the solvent and solution, and w_2 is the mass fraction of the solute in the solution.

In the range of concentrations studied, the variation of V_2^{app} with w_2 is practically linear and V_2^∞ has been obtained by linear extrapolation.

Results

The densities of all the diketones studied in this work and of adamantane in cyclohexane at 298.15 K are shown in Table I. The densities of 1AdDKMe and 1AdDKBu^t have also been determined in bezene at 298.15 K. These results are given in Table II.

Table III summarizes the experimental values of the partial molar volume, V_2^∞, for all the compounds studied, calculated

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[†] Universidad Complutense.

[‡] Universidad Politécnica.

[§] Universitat Autònoma de Barcelona.

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Table I. Densities for Diketones (2) or adamantane (2) + cyclohexane (1) at 298.15 K

1AdDKMe		1AdDKBu^t		1AdMeDKMe		2AdDKMe		adamantane	
10^3w_2	$10^{-3}\rho/(\mathrm{kg{\cdot}m^{-3}})$	10^3w_2	$10^{-3}\rho/(\mathrm{kg{\cdot}m^{-3}})$	10^3w_2	$10^{-3}\rho/(\mathrm{kg{\cdot}m^{-3}})$	10^3w_2	$10^{-3}\rho/(\mathrm{kg{\cdot}m^{-3}})$	10^3w_2	$10^{-3}\rho/(\mathrm{kg{\cdot}m^{-3}})$
1.029	0.774 07	0.992	0.774 10	1.001	0.774 12	0.906	0.774 09	1.027	0.774 05
2.050	0.774 30	1.981	0.774 29	1.986	0.774 35	2.056	0.774 33	2.026	0.774 21
4.043	0.774 72	2.960	0.774 48	2.980	0.774 57	2.761	0.774 46	3.038	0.774 37
5.041	0.774 95	3.964	0.774 68	4.033	0.774 79	3.820	0.774 69	4.065	0.774 54
6.110	0.775 19	4.979	0.774 87	4.972	0.775 01	4.340	0.774 80	4.986	0.774 69
7.107	0.775 38	5.971	0.775 07	5.982	0.775 24	5.291	0.775 00	6.058	0.774 86
8.212	0.775 64					5.816	0.775 11		

Table II. Densities of Compound 1AdDKMe (2) and 1AdDKBu^t (2) + benzene (1) at 298.15 K

1AdDKMe		1AdDKBu^t	
10^3w_2	$10^{-3}\rho/(\mathrm{kg{\cdot}m^{-3}})$	10^3w_2	$10^{-3}\rho/(\mathrm{kg{\cdot}m^{-3}})$
2.070	0.874 00	3.147	0.874 00
2.937	0.874 14	4.243	0.874 15
4.052	0.874 34	5.402	0.874 30
4.952	0.874 49	6.676	0.874 50
6.085	0.874 70		

Table III. Experimental Partial Molar Volume, V_2^∞, and Partial Molar Volume Calculated by Group Contributions, $(V_2^\infty)_{gc}$, of α-Adamantyl β-Diketones and Adamantane at 298.15 K

	$V_2^\infty/(\mathrm{cm^3{\cdot}mol^{-1}})$		
compound	cyclohexane	benzene	$(V_2^\infty)_{gc}/(\mathrm{cm^3{\cdot}mol^{-1}})$
1AdDKMe	217.2 ± 2.4	215.1 ± 1.9	210.0
1AdDKBu^t	306.6 ± 1.8	308.7 ± 11.6	305.6
1AdMeDKMe	225.4 ± 2.6		225.3
2AdDKMe	216.7 ± 1.8		211.1
adamantane	139.1 ± 0.7		140.6

from the linear extrapolation to $w_2 \rightarrow 0$ of V_2^{app} obtained using eq 1. In this table the values of the partial molar volume determined by group contributions given by Fedors (*7*) have also been included.

Discussion

There is good agreement between our value of V_2^∞ for adamantane in cyclohexane solution at 298.15 K and the bibliographic results in the same conditions of measurement ($V_2^\infty = 138.7$ cm^3 mol^{-1}) (*5, 6*).

From the results of the partial molar volume, V_2^∞, for the α-adamantyl β-diketones studied, we make the following conclusions.

There is no change in the value of the partial molar volume when the attaching position of the adamantyl group is modified.

In compound 1AdDKBu^t the value of the partial molar volume is 41% greater compared to that of compound 1AdDKMe. This is due to the higher volume and steric hindrance that the *tert*-butyl group introduces in the molecule.

For compounds 1AdDKMe and 1AdDKBu^t the value of V_2^∞ is independent of solvent. Both values are in good agreement with the one obtained by group contribution.

The substitution of the hydrogen atom for a methyl group in the intercarbonyl position in compound 1AdMeDKMe in relation to compound 1AdDKMe does not significantly affect V_2^∞.

There is good agreement between the experimental partial molar volume of adamantane and α-adamantyl β-diketones and the same magnitude calculated by group contributions. In all the cases the differences are less than 4%. This result is in good agreement with the estimated error of the Fedors method.

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