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Apparent and Partial Molar Volumes at Infinite Dilution and Solid−Liquid Equilibria of Dibenzothiophene + Alkane Systems

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Supporting Information

ABSTRACT: Densities of binary mixtures of dibenzothiophene (DBT), 4-methyl-dibenzothiophene (4-MDBT), or 4,6-dimethyl-dibenzothiophene (4,6-DMDBT) with alkanes were measured at T = (298.2 and 313.2) K. Apparent molar volumes V_ϕ and partial molar volume at infinite dilution $\overline{V}^\infty$ of solutes were obtained, respectively, by experiments and by fitting V_ϕ data to the Redlich−Meyer equation. $\overline{V}^\infty$ increases with the solvent chain length for DBT solutions in linear alkanes, reaching a limiting value of 149.5 $\text{cm}^3\cdot\text{mol}^{-1}$ at 298.2 K; the alkylation of the DBT molecule in positions 4 and 6 also increases $\overline{V}^\infty$. The infinite dilution transference volume $\Delta\overline{V}_{\text{tr}}^\infty$ from cyclohexane to *n*-hexane is −10 $\text{cm}^3\cdot\text{mol}^{-1}$ at T = 298.2 K, and from iso-octane to *n*-octane the transference volumes are (1.4 and 4.3) $\text{cm}^3\cdot\text{mol}^{-1}$ at T = (298.2 and 313.2) K, respectively. Solid−liquid equilibrium data for the same binary mixtures were determined. At 298.2 K, the maximum solubility of DBT in linear alkanes increases with solvent chain length, is greater in cyclohexane than in *n*-hexane, and is lower in iso-octane than in *n*-octane. For studied solutes, the maximum solubility in *n*-dodecane has the following order: 4,6-DMDBT < DBT < 4-MDBT.

INTRODUCTION

Thermodynamic properties, especially volumetric, for binary mixtures involving organic molecular compounds are interesting for process design and knowledge of molecular interactions. Molar volumes are among the most often determined properties of binary mixtures.[1] To know the solute−solute and solute−solvent interaction behavior, the partial molar properties of dilute solutions are significant. In literature, there are works presenting volumetric properties of aqueous solutions of salts,[2,3] carbohydrates,[4,5] alcohols,[6,7] amino acids,[8,9] ionic liquids,[10,11] amines, and polymers.[12,13] Also, studies have been reported on partial molar volumes of solutions in nonpolar solvents.[14−17] Such results can contribute to clarify intermolecular interactions that exists between different species in solution.

In desulfurization of fuels, the class of sulfur contaminants most difficult to remove by the conventional process of hydrodesulfurization is the dibenzothiophene (DBT) derivatives, which includes DBT itself, 4-methyl-dibenzothiophene (4-MDBT), and 4,6-dimethyl-dibenzothiophene (4,6-DMDBT).[18,19]

As part of an experimental study aimed at the desulfurization of model fuels by liquid extraction,[20−22] here density, ρ, measurements and solid−liquid equilibrium (SLE) data for binary liquid mixtures of DBT + {C_5 to C_{12} alkanes} and {4-MDBT or 4,6-DMDBT} + *n*-dodecane at T = (298.2 and 313.2) K are reported. From these data, the solute apparent molar volume V_ϕ and infinite dilution partial molar volume $\overline{V}_1^\infty$ were obtained. Furthermore, data on volumetric behavior of DBT solutions in alkanes are scarce. Recently, Martínez and coauthors[23] have reported the solubility of DBT in *n*-propane.

EXPERIMENTAL SECTION

Chemicals. The properties of chemicals used are listed in Table 1. Comparing density at 298.2 K and at 313.2 K obtained in this work with literature values, a deviation of 0.0001 $\text{g}\cdot\text{cm}^{-3}$ is obtained. The chemical structures of DBTs used here are shown in Figure 1.

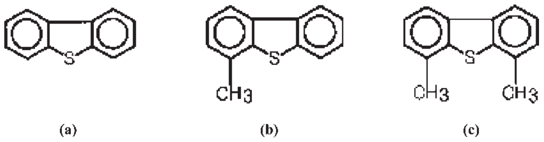

Figure 1. Chemical structures of (a) DBT, (b) 4-MDBT, and (c) 4,6-DMDBT. Source: Kwak et al.[19]

Apparatus and Procedure. To determine apparent molar volumes of binary mixtures of DBTs and alkanes, initially the compounds were weighed in a Shimadzu AX200 analytical balance (precise to ± $1\cdot10^{-4}$ g), directly inside glass vials to avoid loss of mass, and agitated with a Fisatom 152 magnetic stirrer until complete dissolution of the solute. Densities of the pure alkanes and their mixtures with DBTs were measured in an Anton Paar DMA 5000 U-tube vibration densimeter (precise to ± $1\cdot10^{-6}$ $\text{g}\cdot\text{cm}^{-3}$). The uncertainty of density measurement is ± $5\cdot10^{-5}$ $\text{g}\cdot\text{cm}^{-3}$.

As described elsewhere,[21] in the SLE experiments, mixtures of DBTs + alkanes were prepared inside equilibrium cells connected to a thermostatic bath (precise to ± 0.1 K) and magnetically agitated. In these experiments, DBTs reached saturation in the alkane, and the saturated solution, above the pure component solid phase, was analyzed by calibration curves of density ρ versus to molar fraction x.

RESULTS AND DISCUSSION

Apparent Molar Volumes. The densities of the binary system for DBTs (1) + alkanes (2) at T = (298.2 and 313.2)

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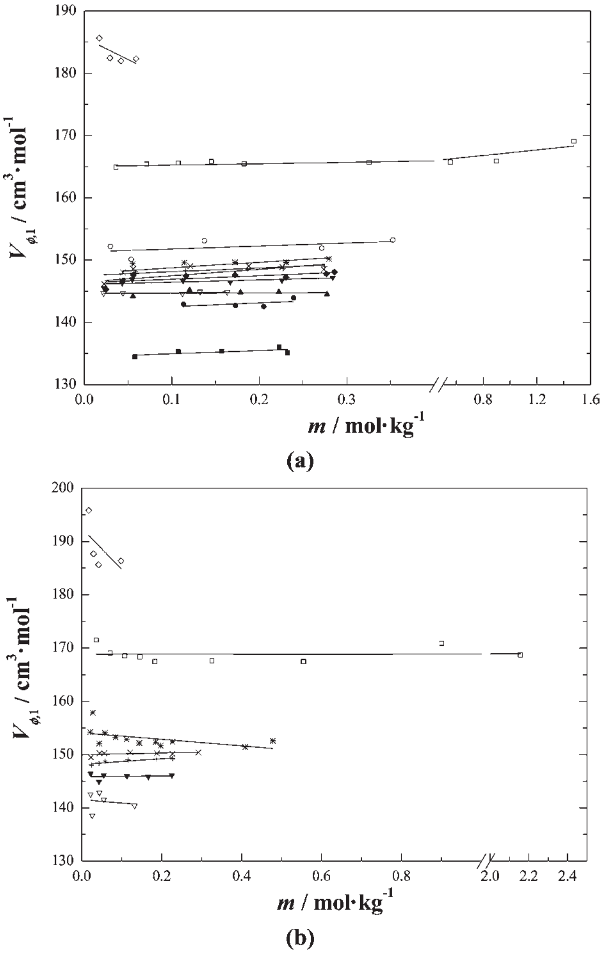
Table 1. Properties of Pure Components

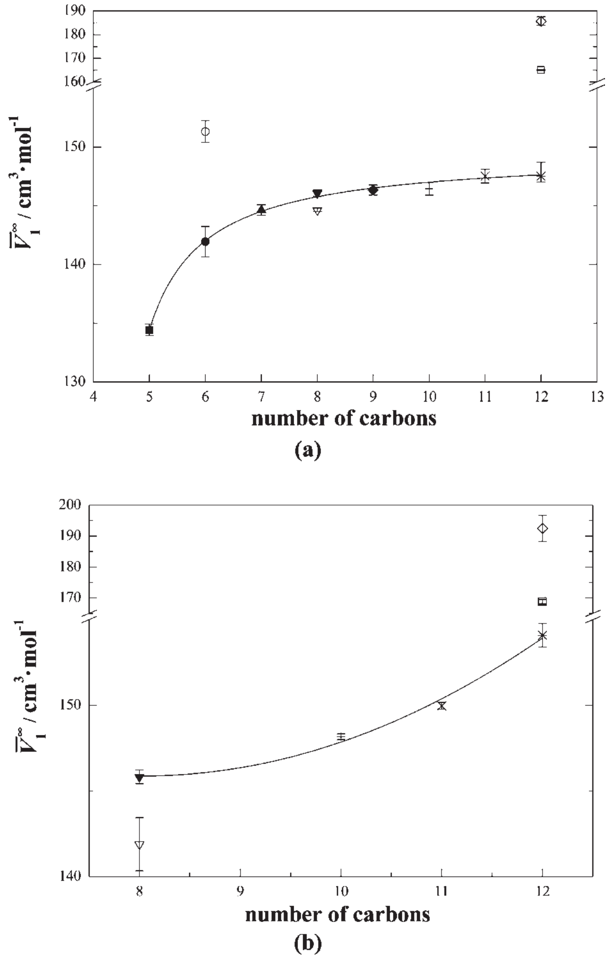
		M	$\rho/(\mathrm{g\cdot cm^{-3}})$					
			T/K = 298.2		T/K = 313.2			
chemical	CAS	$\mathrm{g\cdot mol^{-1}}$	expt	lit.	expt	lit.	purity	supplier
DBT	132-65-0	184.26		1.35[24]			≥0.98	Fluka
4-MDBT	7372-88-5	198.28		1.27[25]			0.96	Aldrich
4,6-DMDBT	1207-12-1	212.31					0.97	Aldrich
n-pentane	109-66-0	72.15	0.621308	0.62135[26]			>0.990	Merck
n-hexane	110-54-3	86.18	0.655039	0.65484[26]			>0.96	Merck
cyclohexane	110-82-7	84.16	0.773849	0.7736[27]			>0.995	Merck
n-heptane	142-82-5	100.21	0.679857	0.67948[26]			>0.99	Sigma
n-octane	111-65-9	114.23	0.698569	0.6986[26]	0.686365	0.6863[28]	>0.97	Spectrum
iso-octane	540-84-1	114.23	0.687721	0.68782[29]	0.675225	0.67538[30]	>0.995	Merck
n-nonane	111-84-2	128.20	0.713938	0.71385[26]			0.99	Aldrich
n-decane	124-18-5	142.29	0.726100	0.7262[26]	0.714726	0.71476[30]	>0.99	Sigma
n-undecane	1120-21-4	156.31	0.736786	0.7369[31]	0.725693	0.7255[32]	>0.99	Aldrich
n-dodecane	112-40-3	170.34	0.745150	0.74532[33]	0.734325	0.73433[30]	0.9960	Fluka



(a)

(b)

Figure 2. Apparent molar volumes V_ϕ of binary mixtures of alkanes + DBTs plotted against molality at (a) T = 298.2 K and (b) T = 313.2 K: ■, *n*-pentane + DBT; ●, *n*-hexane + DBT; ○, cyclohexane + DBT; ▲, *n*-heptane + DBT; ▼, *n*-octane + DBT; ▽, iso-octane + DBT; ♦, *n*-nonane + DBT; +, *n*-decane + DBT; ×, *n*-undecane + DBT; ∗, *n*-dodecane + DBT; □, *n*-dodecane + 4-MDBT; ◇, *n*-dodecane + 4,6-DMDBT; lines are from eq 2.



(a)

(b)

Figure 3. Partial molar volume $\overline{V}_1^\infty$ of alkanes + DBTs plotted against the number of carbons of solvent at (a) T = 298.2 K and (b) T = 313.2 K: ■, *n*-pentane + DBT; ●, *n*-hexane + DBT; ○, cyclohexane + DBT; ▲, *n*-heptane + DBT; ▼, *n*-octane + DBT; ▽, iso-octane + DBT; ♦, *n*-nonane + DBT; +, *n*-decane + DBT; ×, *n*-undecane + DBT; ∗, *n*-dodecane + DBT; □, *n*-dodecane + 4-MDBT; ◇, *n*-dodecane + 4,6-DMDBT; lines are from eq 4 (298.2 K) and 5 (313.2 K); |−|, error bars.

Table 2. Experimental Densities, ρ, and Apparent Molar Volumes, $V_{\phi,1}$, of Binary Mixtures DBT or 4-MDBT or 4,6-DMDBT (1) + Solvents (2) at (298.2 and 313.2) K[a]

		m	$\rho/(\mathrm{g\cdot cm^{-3}})$		$V_{\phi,1}/(\mathrm{cm^3\cdot mol^{-1}})^b$	
solvent	x_1[b]	$\mathrm{mol\cdot kg^{-1}}$	T/K = 298.2	T/K = 313.2	T/K = 298.2	T/K = 313.2
			DBT			
n-pentane	0.0042	0.0582	0.624932		134.48 ± 3.19	
	0.0077	0.1077	0.627957		135.26 ± 1.81	
	0.0112	0.1572	0.630962		135.34 ± 1.19	
	0.0158	0.2228	0.634865		135.99 ± 0.86	
	0.0165 ± 0.0081[c]	**0.2326**	**0.635527**		**135.11 ± 3.42**	
n-hexane	0.0097	0.1136	0.661714		142.90 ± 1.46	
	0.0147	0.1729	0.665156		142.72 ± 0.96	
	0.0174	0.2052	0.667026		142.54 ± 0.89	
	0.0202 ± 0.0002[c]	**0.2393**	**0.668837**		**143.91 ± 0.69**	
cyclohexane	0.0025	0.0301	0.775392		152.20 ± 3.94	
	0.0045	0.0538	0.776667		150.09 ± 2.24	
	0.0114	0.1373	0.780726		153.11 ± 0.87	
	0.0224	0.2717	0.787439		151.92 ± 1.05	
	0.0288 ± 0.0001[c]	**0.3528**	**0.791070**		**153.19 ± 0.34**	
n-heptane	0.0056	0.0558	0.683108		144.23 ± 2.75	
	0.0119	0.1203	0.686774		145.19 ± 1.28	
	0.0176	0.1786	0.690099		144.82 ± 0.86	
	0.0218	0.2225	0.692551		144.87 ± 0.69	
	0.0271 ± 0.0002[c]	**0.2777**	**0.695669**		**144.48 ± 0.67**	
n-octane	0.0026	0.0225	0.699866	0.687657	145.54 ± 6.44	146.45 ± 6.68
	0.0049	0.0435	0.701048	0.688882	146.34 ± 3.34	144.96 ± 3.46
	0.0063	0.0551	0.701696	0.689525	146.91 ± 2.63	146.12 ± 2.73
	0.0127	0.1130	0.704954	0.692813	146.66 ± 1.29	145.98 ± 1.33
	0.0187	0.1670	0.707967	0.695851	146.45 ± 0.87	145.83 ± 0.90
	0.0252	0.2260	0.711182	0.699100	146.75 ± 0.64	146.12 ± 0.67
	0.0314 ± 0.0001[c]	**0.2841**	**0.714273**		**147.20 ± 0.51**	
iso-octane	0.0025	0.0223	0.689019	0.676548	144.67 ± 6.76	142.57 ± 6.98
	0.0030	0.0265		0.676845		138.55 ± 5.89
	0.0050	0.0443	0.690292	0.677841	144.72 ± 3.40	142.87 ± 3.52
	0.0063	0.0551		0.678505		141.55 ± 2.84
	0.0127	0.1125	0.694210		144.60 ± 1.34	
	0.0149	0.1325	0.695329	0.683130	144.93 ± 1.15	140.40 ± 1.18
	0.0183 ± 0.0001[c]	**0.1633**	**0.697078**		**144.84 ± 0.92**	
n-nonane	0.0032	0.0250	0.715374		145.31 ± 5.55	
	0.0057	0.0444	0.716447		146.66 ± 3.13	
	0.0072	0.0564	0.717097		147.57 ± 2.46	
	0.0147	0.1165	0.720427		147.46 ± 1.19	
	0.0216	0.1724	0.723475		147.59 ± 0.81	
	0.0287	0.2307	0.726668		147.22 ± 0.60	
	0.0343	0.2769	0.729068		147.75 ± 0.50	
	0.0354 ± 0.0001[c]	**0.2860**	**0.729503**		**148.07 ± 0.49**	
n-decane	0.0034	0.0239	0.727461	0.716064	145.55 ± 5.62	148.03 ± 5.81
	0.0061	0.0434	0.728541	0.717143	146.62 ± 3.10	148.30 ± 3.20
	0.0082	0.0584	0.729331	0.717957	148.08 ± 2.31	148.76 ± 2.38
	0.0162	0.1159	0.732459	0.721088	148.36 ± 1.16	148.99 ± 1.20
	0.0259	0.1869	0.736262	0.724901	148.58 ± 0.72	149.13 ± 0.74
	0.0314	0.2275	0.738412	0.727044	148.61 ± 0.59	149.26 ± 0.61
	0.0376 ± 0.0002[c]	**0.2748**	**0.740850**		**148.92 ± 0.49**	
n-undecane	0.0035	0.0227	0.738065	0.726939	146.20 ± 5.75	149.51 ± 5.92
	0.0069	0.0444	0.739235	0.728106	148.03 ± 2.95	150.24 ± 3.03

Table 2. Continued

		m	$\rho/(\mathrm{g \cdot cm^{-3}})$		$V_{\phi,1}/(\mathrm{cm^3 \cdot mol^{-1}})$[b]	
solvent	x_1[b]	$\mathrm{mol \cdot kg^{-1}}$	T/K = 298.2	T/K = 313.2	T/K = 298.2	T/K = 313.2
	0.0087	0.0562	0.739863	0.728741	148.57 ± 2.34	150.25 ± 2.40
	0.0186	0.1214	0.743359	0.732220	149.02 ± 1.08	150.46 ± 1.11
	0.0263	0.1726		0.735021		
	0.0286	0.1883	0.746909	0.735767	149.03 ± 0.70	150.25 ± 0.72
	0.0342	0.2266	0.748935	0.737778	148.89 ± 0.58	150.16 ± 0.60
	0.0410 ± 0.0002[c]	**0.2739**	**0.751448**		**148.51 ± 0.48**	
	0.0436	0.2918		0.74111		150.39 ± 0.46
n-dodecane	0.0037	0.0216		0.735448		154.20 ± 6.09
	0.0046	0.0274		0.735694		157.85 ± 4.80
	0.0074	0.0435	0.747569	0.736633	146.69 ± 2.93	152.06 ± 3.02
	0.0094	0.0555	0.748147		149.42 ± 2.30	
	0.0098	0.0580		0.737333		154.07 ± 2.27
	0.0142	0.0849		0.738752		153.25 ± 1.55
	0.0187	0.1121		0.740177		152.88 ± 1.17
	0.0191	0.1144	0.751276		149.60 ± 1.12	
	0.0240	0.1441		0.741874		152.18 ± 0.91
	0.0285	0.1724	0.754322		149.62 ± 0.74	
	0.0305	0.1848		0.743953		152.31 ± 0.71
	0.0325	0.1974		0.744662		151.68 ± 0.67
	0.0372	0.2268		0.746081		152.37 ± 0.58
	0.0378	0.2309	0.757354		149.63 ± 0.55	
	0.0455 ± 0.0001[c]	**0.2798**	**0.759777**		**150.18 ± 0.46**	
	0.0651	0.4090		0.755317		151.41 ± 0.35
	0.0753 ± 0.0003[d]	**0.4779**		**0.758386**		**152.56 ± 0.28**
			4-MDBT			
n-dodecane	0.0062	0.0366	0.747197	0.736260	164.93 ± 3.55	171.51 ± 3.65
	0.0120	0.0712	0.749098	0.738169	165.38 ± 1.83	169.04 ± 1.88
	0.0180	0.1075	0.751069	0.740129	165.60 ± 1.21	168.54 ± 1.25
	0.0242	0.1454	0.753104	0.742156	165.80 ± 0.90	168.34 ± 0.92
	0.0302	0.1826	0.755131	0.744204	165.45 ± 0.72	167.44 ± 0.75
	0.0526	0.3257	0.762606	0.751621	165.70 ± 0.40	167.60 ± 0.41
	0.0863	0.5548	0.774082	0.763057	165.74 ± 0.24	167.42 ± 0.24
	0.1330	0.9005	0.790240	0.777581	165.88 ± 0.15	170.87 ± 0.15
	0.2009 ± 0.0002[c]	**1.4766**	**0.812185**		**169.12 ± 0.09**	
	0.2685	2.1553		0.827245		168.72 ± 0.07
			4,6-DMDBT			
n-dodecane	0.0031	0.0173	0.746102	0.735193	185.63 ± 7.49	195.83 ± 7.69
	0.0053	0.0295	0.74682	0.735931	182.46 ± 4.40	187.65 ± 4.53
	0.0076	0.0422	0.747546	0.736664	182.00 ± 3.08	185.63 ± 3.18
	0.0100 ± 0.0001[c]	**0.0593**	**0.748499**		**182.35 ± 2.19**	
	0.0165 ± 0.0003[d]	**0.0986**		**0.739716**		**186.34 ± 1.45**

[a] Bold values indicate the molar fraction, molality, and density of each saturated solution. [b] Reported in the form: value ± uncertainty. [c] SLE at 298.2 K. [d] SLE at 313.2 K.

K are presented in Table 2. It is verified that mixtures densities increase with the increase of DBT molar fraction in alkane. The apparent molar volumes were calculated by eq 1

$$V_{\phi,1} = \frac{M_1}{\rho} + \frac{1000}{m}\left(\frac{\rho_2 - \rho}{\rho \rho_2}\right) \tag{1}$$

and fitted, as function of molality m, to the Redlich–Meyer equation, eq 2[34]

$$V_{\phi,1} = \overline{V}_1^{\infty} + S_v\sqrt{m} + b_v m \tag{2}$$

used for solutions of nonelectrolytes, when taking $S_v = 0$,[1,16,17,35−39] to obtain the partial molar volume at infinite dilution of DBTs $\overline{V}_1^{\infty}$ in each alkane studied. In eqs 1 and 2,

Table 3. Partial Molar Volume $\overline{V}_1^\infty$, Linear Coefficient b_v, and Regression Standard Deviation σ for Binary Mixtures of DBT or 4-MDBT or 4,6-DMDBT (1) + Solvents (2) at (298.2 and 313.2) K

	T/ K = 298.2			T/ K = 313.2		
	$\overline{V}_1^{\infty a}$	b_v	σ	$\overline{V}_1^{\infty a}$	b_v	σ
solvent	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot kg \cdot mol^{-2}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot kg \cdot mol^{-2}$	$cm^3 \cdot mol^{-1}$
			DBT			
n-pentane	134.44 ± 0.50	5.14	0.44			
n-hexane	141.93 ± 1.30	5.92	0.64			
cyclohexane	151.31 ± 0.93	4.70	1.23			
n-heptane	144.62 ± 0.46	0.54	0.43			
n-octane	146.08 ± 0.28	3.62	0.43	145.83 ± 0.40	0.79	0.56
iso-octane	144.63 ± 0.12	1.23	0.13	141.53 ± 0.62	−6.15	2.01
n-nonane	146.34 ± 0.43	5.74	0.67			
n-decane	146.44 ± 0.53	10.37	0.80	148.16 ± 0.17	5.32	0.23
n-undecane	147.51 ± 0.59	6.09	0.88	149.98 ± 0.20	1.50	0.30
n-dodecane	147.86 ± 0.84	8.90	1.03	154.08 ± 0.69	−6.13	1.55
			4-MDBT			
n-dodecane	165.01 ± 0.13	2.22	0.61	168.81 ± 0.66	0.04	0.87
			4,6-DMDBT			
n-dodecane	185.69 ± 1.80	−69.67	1.40	192.49 ± 4.22	−77.42	4.66

[a] Reported in the form: value ± uncertainty.

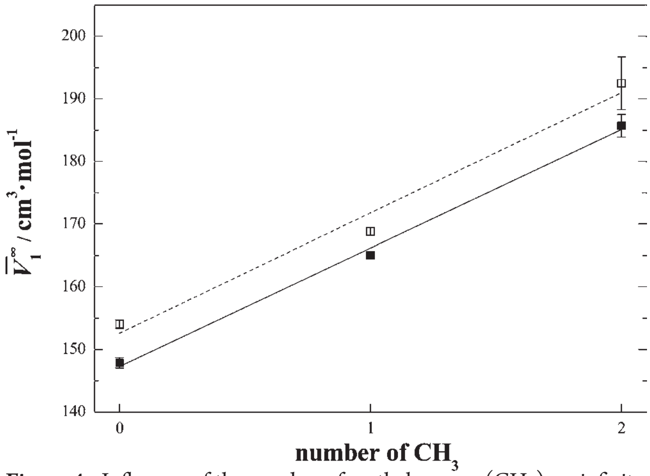


Figure 4. Influence of the number of methyl groups (CH_3) on infinite dilution partial molar volume of DBTs $\overline{V}_1^\infty$ in *n*-dodecane: ■, 298.2 K; □, 313.2 K; |−|, error bars.

$V_{\phi,1}$, M_1, and ρ_2 are the apparent molar volume of the solute, molar mass of the solute, and density of the alkane; S_v and b_v are empirical parameters. The partial molar volume at infinite dilution describes the solute−solvent interactions,[39] and the solute apparent molar volume of nonelectrolyte solutions varies little and is almost linear with the concentration.[4,34,40]

Apparent molar volumes obtained are shown in Table 2, and the parameters of eq 2 ($\overline{V}_1^\infty$ and b_v) are presented in Table 3, together with the fit of the standard deviation σ, given by eq 3

$$\sigma = \left[\frac{\Sigma(P^{\text{calc}} - P^{\text{exp}})^2}{n - p}\right]^{1/2} \qquad (3)$$

Table 4. Equation 7 Coefficients and Standard Deviation σ for Density ρ as a Function of Solute Molar Fraction x

	T/ K = 298.2			T/ K = 313.2 K		
	A''	B''	$10^5 \cdot \sigma$	A''	B''	$10^5 \cdot \sigma$
alkane	$g \cdot cm^{-3}$	$g \cdot cm^{-3}$	$g \cdot cm^{-3}$	$g \cdot cm^{-3}$	$g \cdot cm^{-3}$	$g \cdot cm^{-3}$
			DBT			
n-pentane	0.6213	0.8569	2.7			
n-hexane	0.6550	0.6897	0.9			
cyclohexane	0.7739	0.6062	5.7			
n-heptane	0.6799	0.5818	1.4			
n-octane	0.6986	0.5014	1.0	0.6864	0.5063	1.1
iso-octane	0.6877	0.5107	0.7	0.6752	0.5302	3.0
n-nonane	0.7139	0.4417	2.1			
n-decane	0.7261	0.3918	1.6	0.7147	0.3926	0.5
n-undecane	0.7368	0.3543	2.0	0.7257	0.3535	2.1
n-dodecane	0.7452	0.3218	3.2	0.7342	0.3219	8.1
			4-MDBT			
n-dodecane	0.7450	0.3387	14.7	0.7338	0.3440	84.7
			4,6-DMDBT			
n-dodecane	0.7451	0.3146	2.1	0.7343	0.3079	5.5

where P, n, and p represent the property studied, the number of experimental data, and parameters, respectively.

In Figure 2 the apparent molar volumes against molality of DBT at (298.2 and 313.2) K are plotted, together with each linear regression line calculated by eq 2. In Figure 3, the infinite dilution partial molar volume of DBT is plotted against the carbon number of the solvent (n_c). At 298.2 K, $\overline{V}_1^\infty$ increase from C_5

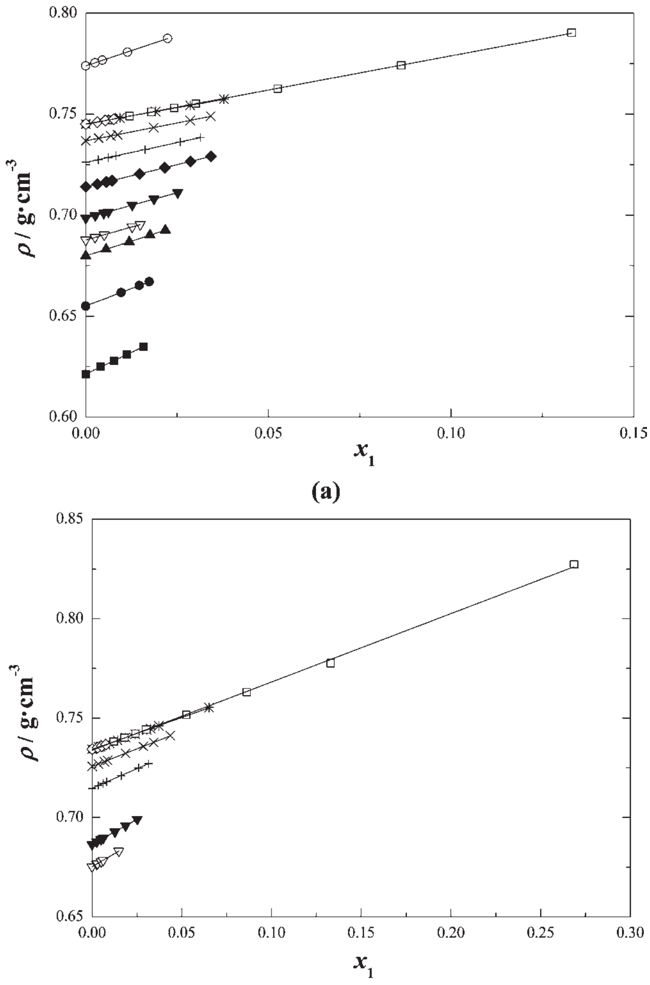


Figure 5. Density ρ of binary mixtures of alkanes + DBTs plotted against the molar fraction of solute at (a) $T = 298.2$ K and (b) $T = 313.2$ K: ■, *n*-pentane + DBT; ●, *n*-hexane + DBT; ○, cyclohexane + DBT; ▲, *n*-heptane + DBT; ▼, *n*-octane + DBT; ▽, iso-octane + DBT; ♦, *n*-nonane + DBT; +, *n*-decane + DBT; ×, *n*-undecane + DBT; ∗, *n*-dodecane + DBT; □, *n*-dodecane + 4-MDBT; ◊, *n*-dodecane + 4,6-DMDBT; lines are from eq 7.

to C_9, reaching a constant value for alkanes of superior chain lengths. The limiting value was calculated by fitting eq 4 to these data.

$$\overline{V}_1^{\infty} = A + \frac{B}{C + n_c} \tag{4}$$

Adjusted parameters *A*, *B*, and *C* obtained are equal to (149.47, −14.74, and −4.02) $\text{cm}^3 \cdot \text{mol}^{-1}$, respectively. The standard deviation for this fit is equal to 0.33 $\text{cm}^3 \cdot \text{mol}^{-1}$.

The value of parameter *A* is the limiting value of $\overline{V}_1^{\infty}$ as a function of carbon number of the solvent at 298.2 K. It demonstrates that the infinite dilution interactions of solute—solvent do not depend on chain length for higher alkanes. At 313.2 K, $\overline{V}_1^{\infty}$ increase in the range of C_8 to C_{12} without reaching a limiting value. A study of these solutions for alkanes higher than C_{12} would give a better visualization of the behavior at 313.2 K. These data were fitted to eq 5 to qualitatively show the behavior in the C_8 to C_{12} range.

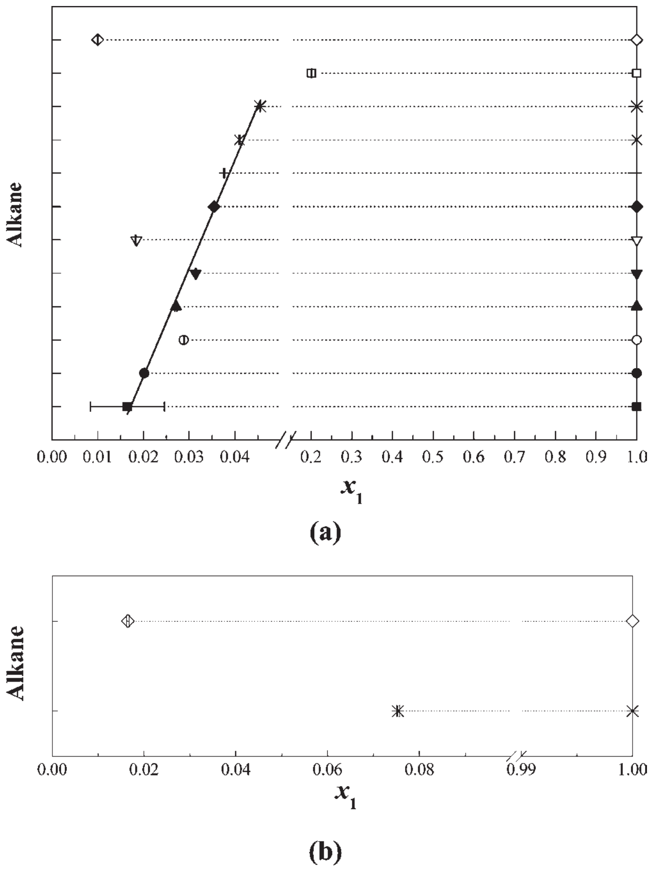


Figure 6. SLE data (dotted lines) in molar fraction for binary solutions of alkanes + DBTs at (a) $T = 298.2$ K and (b) $T = 313.2$ K: ■, *n*-pentane + DBT; ●, *n*-hexane + DBT; ○, cyclohexane + DBT; ▲, *n*-heptane + DBT; ▼, *n*-octane + DBT; ▽, iso-octane + DBT; ♦, *n*-nonane + DBT; +, *n*-decane + DBT; ×, *n*-undecane + DBT; ∗, *n*-dodecane + DBT; □, *n*-dodecane + 4-MDBT; ◊, *n*-dodecane + 4,6-DMDBT; the solid line shows the linear increase of DBT solubility in linear alkanes; |—|, error bars.

$$\overline{V}_1^{\infty} = A' + B'n_c + C'n_c^{\,2} \tag{5}$$

A', B', and C' are adjusted parameters equal to (178.9, −8.22, and 0.51) $\text{cm}^3 \cdot \text{mol}^{-1}$, respectively. The standard deviation for this fit is equal to 0.53 $\text{cm}^3 \cdot \text{mol}^{-1}$. For both temperatures, $\overline{V}_1^{\infty}$ increases with the chain length of alkane; it shows that solute—solvent conformation interactions become smaller.

To investigate the influence of methyl groups bonded to DBT on V_ϕ and $\overline{V}^{\infty}$, the density of {4-MDBT or 4,6-DMDBT} + *n*-dodecane was determined, and the results are also shown in Tables 2 and 3 and Figures 2 and 3.

V_ϕ and $\overline{V}^{\infty}$ of *n*-dodecane solutions obtained for these alkyl-DBTs are greater than those for DBT. The presence of a methyl at the 4- and 4,6-positions increase linearly $\overline{V}^{\infty}$ in the order DBT < 4-MDBT < 4,6-DMDBT, and the increase in temperature gives an increase in $\overline{V}^{\infty}$ (see Figure 4). As DBT molecule becomes more alkylated, its volume enlarges, and $\overline{V}^{\infty}$ increases. Also, an increase in temperature makes solute and solvent molecules to separate, diminishing the density and increasing $\overline{V}^{\infty}$.

For nonlinear solvents studied (cyclohexane and iso-octane), V_ϕ and $\overline{V}^{\infty}$ values do not have the same tendencies of linear alkanes. For cyclohexane, the V_ϕ and $\overline{V}^\infty$ values are even greater than for *n*-dodecane. For iso-octane, these values are in the order of *n*-octane at 298.2 K and slightly below at 313.2 K. These results can be explained by the transference volume of a solute between two solvents $\Delta\overline{V}^\infty_{1,\mathrm{tr}}(\text{solvent 1}\rightarrow\text{solvent 2})$, which is calculated by eq 6.[16]

$$\Delta\overline{V}^\infty_{1,\mathrm{tr}}(\text{solvent 1} \rightarrow \text{solvent 2}) = \overline{V}^\infty_1(\text{solvent 2}) - \overline{V}^\infty_1(\text{solvent 1}) \quad (6)$$

For DBT, at 298.2 K, the transference volume from cyclohexane to *n*-hexane is $-10\ \mathrm{cm^3 \cdot mol^{-1}}$; from iso-octane to *n*-octane the transference volumes are (1.4 and 4.3) $\mathrm{cm^3 \cdot mol^{-1}}$ at T = (298.2 and 313.2) K, respectively. These results indicate a specific steric arrangement of DBT in these nonlinear C6 and C8 alkanes. They present opposite behavior: although both nonlinear solvents are more spherical (smaller acentric factors) than the corresponding linear alkane, cyclohexane increases the partial molar volume, and iso-octane decreases. This probably occurs due to better DBT solvation by iso-octane.

SLE Data. The mixture densities for each system present in Table 2 were fit to eq 7,

$$\rho = A'' + B''x_1 \quad (7)$$

and the parameters A'' and B'', together with standard deviations calculated by eq 3, are shown in Table 4. Experimental and calculated densities as a function of molar fraction are presented in Figure 5. Equation 7 was used to calculate the molar fraction of a saturated solution in equilibrium with solid DBT not dissolved in the alkane, measuring the density values of these solutions. The values in bold in Table 2 refer to the molar fraction, molality, and density of each saturated solution. The tie lines connecting the saturated solution to pure DBT are shown in Figure 6.

The effect of chain length of linear alkanes in SLE, that is, in the maximum solubility of DBTs, is presented as a straight line in Figure 6. This linear behavior does not consider the nonlinear solvents and the alkylated DBTs. Comparing the solubility of DBT in cyclohexane and iso-octane, at 298.2 K, to the other solvents, the first presents a DBT molar fraction at SLE between *n*-heptane and *n*-octane and the second, between *n*-pentane and *n*-hexane.

For 4-MDBT and 4,6-DMDBT, at both temperatures, the maximum solubility of solute in *n*-dodecane increases in the order 4,6-DMDBT < DBT < 4-MDBT. For DBT or 4,6-DMDBT, an increase from (298.2 to 313.2) K increases the maximum solubility of these compounds by approximately 65 % (see Table 2). SLE data for 4-MDBT at 313.2 K were not determined due to high cost of this chemical, but it is evident from Table 2 that this compound solubilizes more than DBT at this temperature. Using the same percent (65 %) to estimate the maximum solubility of 4-MDBT at 313.2 K, a value of $x_1 \approx 0.31$ is obtained (this is not shown in Figure 6b). These results match the ones previously obtained by Oliveira and Aznar[20−22] using refractometry instead of densimetry. It is hard to explain why the presence of a methyl in 4-MDBT increases the solubility of this compound in *n*-dodecane so much compared to DBT, once 4,6-DMDBT, with two methyl groups, has its solubility diminished. The authors believe that one explanation for this is that the 4-MDBT molecule has a more acentric structure than DBT and 4,6-DMDBT, interacting more easily with *n*-dodecane at concentrated solutions.

The equations used for the calculation of uncertainties in apparent molar volume, infinite dilution molar volume, and saturation solubility of DBT in alkane are reported as Supporting Information.

CONCLUSION

Densities of DBTs with alkanes were measured at T = (298.2 and 313.2) K. The apparent molar volumes and partial molar volume at infinite dilution of solutes were obtained. $\overline{V}^\infty$ increases with the solvent chain length for DBT solutions in linear alkanes, reaching a limiting value of 149.47 $\mathrm{cm^3 \cdot mol^{-1}}$ at 298.2 K; the alkylation of DBT molecule in positions 4 and 6 also increases $\overline{V}^\infty$. The infinite dilution transference volume from cyclohexane to *n*-hexane and iso-octane from *n*-octane can show that, between C8 alkanes, the DBT molecule is more solvated by the nonlinear alkane, and that the contrary occurs with C6 alkanes. Solid—liquid equilibrium data for the same binary mixtures were determined at 298.2 K for C_5 to C_{12} alkanes and at 313.2 K for *n*-dodecane only. The maximum solubility of DBT in linear alkanes increases linearly with solvent chain length; it is greater in cyclohexane than in *n*-hexane and is lower in iso-octane than in *n*-octane. For studied solutes, the maximum solubility in *n*-dodecane has the following order: 4,6-DMDBT < DBT < 4-MDBT. Also, for DBT or 4,6-DMDBT, an increase from (298.2 to 313.2) K increases the maximum solubility of these compounds by approximately 65 %.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Set of equations used for the calculation of uncertainty in apparent molar volume, infinite dilution molar volume, and saturation solubility of solute. This material is available free of charge via the Internet at http://pubs.acs.org.

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