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Solubilities at High Dilution of Toluene, Ethylbenzene, 1,2,4-Trimethylbenzene, and Hexane in Di-2-ethylhexyl, Diisoheptyl, and Diisononyl Phthalates

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Henry's constants of toluene, ethylbenzene (EtB), 1,2,4-trimethylbenzene (TMB), and hexane in di-2-ethylhexyl phthalate (DEHP), diisoheptyl phthalate (DIHP), and diisononyl phthalate (DINP) were determined experimentally applying a dynamic method, at temperatures ranging from (293.15 to 373.15) K and at 1 atm. The logarithms of Henry's constants were fitted as linear functions of the inverse of absolute temperature (thanks to equations similar to the van't Hoff equation). These equilibrium data were predicted with a mean relative deviation of 11 % by the modified UNIFAC thermodynamic model of solution.

Introduction

This paper presents the first experimental part of a general study devoted to the design of a regenerative VOC (volatile organic compounds, involving vapor pressures greater than 10 Pa at 293.15 K) absorption process using heavy solvents as scrubbing agents. The knowledge of the solubilities of a gaseous compound in liquid solvents is essential as well for the solvent selection as for the design of gas−liquid contactors. The solubility data, at a given temperature, for different partial pressures of the solute in the gas phase are generally fitted by Henry's law, applicable for very dilute solutions and near atmospheric pressure.

Many techniques[1] have been investigated and developed to determine the Henry's constants or the activity coefficients at infinite dilution. A quite simple direct and dynamic technique was chosen here consisting of the saturation of a known absorbent volume in continuous contact with a VOC-containing gas of constant concentration.

Our literature review concerning the solubilities of hydrocarbons in phthalates highlighted that a lack of data still exists concerning the systems of VOC−phthalate and temperatures investigated. Alessi et al.[2] determined activity coefficients at infinite dilution for 14 hydrocarbons including toluene, EtB, and hexane in 8 phthalates including DEHP, by gas chromatography at (298.15, 323.15, 348.15, and 373.15) K. Weisweiler and Winterbauer[3] studied the solubility of toluene, EtB, and hexane in DEHP and DIHP at 308.15 K (for the three VOC) and 343.15 K (only for the two first) by headspace gas chromatography.

Experimental Section

Chemicals. All chemical products were of analytical grade and had purities of 99.5 %, 99.8 %, 98 %, and 99 % for toluene, EtB, TMB, and hexane, respectively, and 98 % for all phthalates. Volatile organic compounds were purchased from Acros Organics. DIHP and DINP were obtained from Aldrich, whereas DEHP was provided by Acros Organics.

Table 1. CASRN,[a] Molecular Formula, Molar Mass *M*, Density ρ, and Vapor Pressure P^{sat} at 293.15 K for the VOC

VOC	CASRN	molecular formula	M / kg·mol^{-1}	ρ / kg·m^{-3}	P^{sat} / kPa
hexane	110-54-3	C_6H_{14}	0.08619	659	16.15
toluene	108-88-3	C_7H_8	0.09214	865	2.92
EtB	100-41-4	C_8H_{10}	0.10616	867	0.95
TMB	95-63-6	C_9H_{12}	0.12019	899	0.21

[a] CASRN, Chemical Abstracts Service Registry Number.

Table 2. CASRN, Molecular Formula, Molar Mass *M*, Density ρ, and Viscosity η at 293.15 K for the Phthalates

phthalate	CASRN	molecular formula	M / kg·mol^{-1}	ρ / kg·m^{-3}	η / Pa·s
DIHP	71888-89-6	$C_{22}H_{34}O_4$	0.3625	990	0.045
DEHP	117-81-7	$C_{24}H_{38}O_4$	0.3906	983	0.076
DINP	68515-48-0	$C_{26}H_{42}O_4$	0.4206	972	0.097

Tables 1 and 2 give some important properties of VOC and phthalates used in our experiments. The vapor pressures of VOC were estimated using the Wagner equation.[4] The densities of the VOC were given by the manufacturers. The densities and viscosities of the phthalates were measured experimentally using a densimeter (VWR International) and a falling sphere viscosimeter (Gebrüder Haake K.G.), respectively.

Apparatus and Procedure. The applied dynamic method was based on the saturation of a weighted quantity of phthalate brought continuously in contact with a polluted air, the VOC concentration of which was fixed to a constant value. The experimental apparatus is shown in Figure 1. It is rather similar to that already used by Cotte et al.[5] for the measurement of solubilities of odorous VOC in aqueous solutions of polyethylene glycol.

Experiments were carried out within a 0.25 L thermostatic cell where the carrying air, fed at 1 L·min^{-1} with an inlet VOC concentration of $0.5 \cdot 10^{-3}$ kg·m^{-3}, was bubbled into a heavy solvent volume of 0.1 L, at different temperatures from (293.15 to 373.15) K. The bubbler, placed in a thermostatic bath, was equipped with a grade no. 1 sintered glass having a pore diameter of (100 to 160) μm.

A precise rate of VOC was injected by a syringe dispenser in a dry air stream of 10 L·min^{-1}, whose flow rate was measured

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Table 3. Main Characteristics of Experimental Components

equipment	characteristics	(full) scale	precision
balance	Sartorius	6.2 kg	$0.01 \cdot 10^{-3}$ kg
mass flow controller	Brooks 5880 TR, Holland	20 $\text{L} \cdot \text{min}^{-1}$	1 %
thermostatic bath	Huber	(293 to 373) K	0.5 K
temperature sensor	Testo type K 925	(223 to 1273) K	(223 to 473) K: 0.1 K (473 to 1273) K: 1 K
automatic syringe dispenser	Harvard apparatus	0.22 $\text{L} \cdot \text{min}^{-1}$	0.35 %
syringes	Hamilton TLL	0.01 L	
rotameter	Platon	2 $\text{L} \cdot \text{min}^{-1}$	0.025 $\text{L} \cdot \text{min}^{-1}$

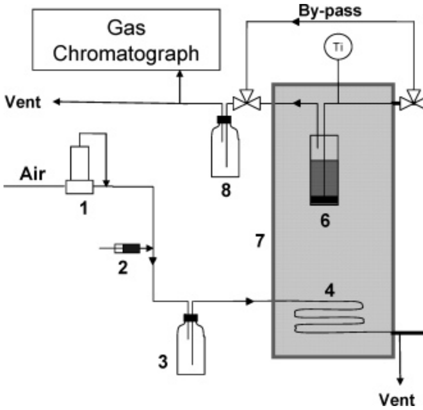

Figure 1. Experimental apparatus: 1, gas mass-flow controller; 2, syringe/syringe dispenser; 3, buffer volume; 4, heat exchange coil; 5, rotameter; 6, bubbler; 7, thermostatic bath; 8, safety volume.

and controlled by a gas mass-flow controller. The air−VOC mixture flowed through a buffer volume of 0.5 L for homogenization and a heat exchange coil immersed in the thermostatic bath. The gas temperature was registered by a temperature sensor. A rotameter, upstream of the cell, allowed us to measure the gas rate (1 $\text{L} \cdot \text{min}^{-1}$) entering the bubbler. Two three-way valves allowed us to direct the mixture toward the bypass, which was useful for the determination of the initial VOC concentration in the inlet gas or the bubbler. A safety volume of 0.5 L, downstream of the bubbler, was installed to avoid damage on chromatograph.

Analytical Method. The gas analysis, upstream and downstream of the absorption cell, was performed by a gas-phase chromatography (Varian CP-2003 Micro-GC) equipped with a thermal conductivity detector (TCD) and a CP-WAX 52CB column.

Measurement Precision. Experimental errors are related to the precision of temperature, flow, and volume measurements. The characteristics of the different parts of the equipment are detailed in Table 3.

Mathematical Approach. The VOC concentration in the liquid phase at any time was computed from the mass balance between the quantities of volatile compound entering and leaving the bubbler. The instantaneous mass balance is given by

$$QC_{G0} = QC_G(t) + V\frac{dC_L}{dt} \tag{1}$$

where Q is the gas flow rate; V is the volume of phthalate; C_{G0} and $C_G(t)$ are the VOC concentrations in the gas at the inlet and the outlet of the bubbler, respectively; and $C_L(t)$ is the concentration of the phthalate. Q, V, and C_{G0} are constant with time while C_G and C_L are time-dependent parameters.

Integration of eq 1 leads to

$$C_L(t) = \frac{Q}{V}\left(C_{G0}t - \int_0^t C_G(t)\,dt\right) \tag{2}$$

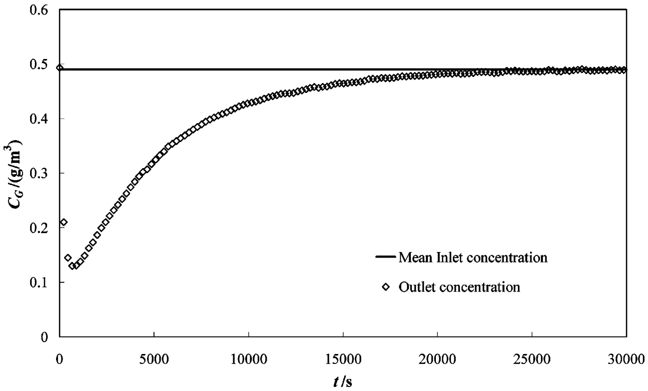

Figure 2. VOC concentration in gas phase (system EtB-DINP at 348.75 K).

$C_L(t)$ reaches a maximum limit, equal to the saturation concentration C_{sat} corresponding to the solubility for the used C_{G0} and temperature. $\int_0^t C_G(t)\,dt$ represents the VOC quantity that is not absorbed in the liquid. This quantity is determined by numerical integration according to the trapezoidal rule, applied to the curve (Figure 2).

Finally, assuming that the gas phase near atmospheric pressure obeys the law of ideal gases, the Henry's constant was determined by

$$p_{VOC} = Hx_{sat} \tag{3}$$

where p_{VOC} is the VOC partial pressure, H is the Henry's constant, and x_{sat} is the molar fraction of dissolved VOC in the solvent, calculated from the saturation concentration C_{sat}. From activity coefficients at infinite dilution given in the literature, Henry's constants were calculated by the following relation:

$$H = P^{sat}\gamma^{\infty} \tag{4}$$

where P^{sat} is the saturation pressure of VOC at the given temperature.

Results and Discussion

Experimental Results. Henry's constants of toluene, EtB, TMB, and hexane in DEHP, DIHP, and DINP at various temperatures (293.15, 308.15, 323.15, 348.15, and 373.15) K and near atmospheric pressure are reported in Table 4. Several measures were reproduced with deviations in results lower than 5 %. As shown in Figures 3 and 4, our experimental results are in satisfactory agreement with those published.[2,3] This finding allowed the validation of our experimental setup and procedure.

Taking account of estimated relative errors of 0.5 % on the phthalate volume measurement, of 2.24 % on the VOC concentration generation, and of 4.57 % on the liquid saturation concentration, a mean relative error on the Henry's constant of 6.9 % was obtained.

As expected, our results clearly show that the solubilities of the different VOC in all phthalates increase (the Henry's constants decrease) with decreasing volatility and decreasing temperature. Figures 3 to 5 clearly show that a linear variation

Table 4. Deviations between Predicted and Experimental Henry's Constants

			H/kPa		deviation	*H*/kPa	deviation	*H*/kPa	deviation
solvent	VOC	*T*/K	UNIFAC DMD	experimental	%	Alessi et al.[2]	%	Weisweiler et al.[3]	%
DIHP	hexane	291.65	26.49	26.32	0.62				
		308.15	51.05	52.61	−2.95			31.15	63.91
		323.15	86.19	89.38	−3.57				
		348.15	182.0	184.1	−1.13				
		373.15	338.8	477.6	−29.05				
	toluene	291.65	1.941	1.814	7.01				
		305.15	4.472	4.874	-8.25			4.398	1.69
		323.15	8.687	9.666	−10.13				
		343.15	15.05					28.25	−46.71
		348.15	22.24	25.00	−11.04				
		373.15	48.03	55.60	−13.61				
	EtB	293.15	0.851	0.689	23.51				
		308.15	1.972	1.895	4.09			1.743	13.17
		323.15	4.139	3.931	5.27				
		343.15	9.756					12.90	−24.36
		348.15	11.84	12.40	−4.50				
		373.15	28.14	30.52	−7.81				
	TMB	323.15	1.022	1.135	−9.92				
		373.15	8.220	9.231	−10.95				
DEHP	hexane	292.15	24.13	29.99	−19.55				
		298.15	30.98			31.61	−1.99		
		308.15	45.75	48.74	−6.14			31.24	46.44
		323.15	77.55	87.02	−10.88	75.15	3.20		
		348.15	164.8	185.5	−11.18	164.1	0.45		
		373.15	308.4	408.0	−24.42	322.0	−4.21		
	toluene	291.65	1.851	1.672	10.73				
		298.15	2.609			2.827	−7.73		
		308.15	4.263	4.499	−5.23			3.881	9.86
		323.15	8.277	8.977	−7.80	8.461	−2.17		
		343.15	17.81					26.64	−33.14
		348.15	21.17	23.71	−10.69	21.77	−2.76		
		363.15	34.22	40.18	−14.82				
		373.15	45.75	57.96	−21.07	49.08	−6.79		
	EtB	291.65	0.733	0.740	−0.96				
		298.15	1.074			0.993	8.16		
		308.15	1.859	2.027	−8.29			1.611	15.36
		323.15	3.901	3.253	19.93	3.334	17.01		
		343.15	9.198					11.74	−21.67
		348.15	11.17	11.88	−5.95	9.514	17.38		
		373.15	26.55	27.94	−4.94	23.38	13.60		
	TMB	293.15	0.168	0.193	−12.53				
		323.15	0.960	1.094	−12.31				
		348.15	3.037	3.627	−16.28				
		373.15	7.810	10.34	−24.43				
DINP	hexane	291.65	21.44	24.19	−11.36				
		308.15	41.62	41.74	−0.27				
		323.15	70.81	62.87	12.63				
		348.15	151.2	200.5	−24.58				
		373.15	284.1	408.2	−30.41				
	toluene	291.65	1.776	1.753	1.34				
		308.15	4.086	4.104	−0.42				
		323.15	7.927	7.893	0.42				
		348.15	20.26	22.25	−8.94				
		373.15	43.77	50.32	−13.00				
	EtB	308.15	1.765	1.500	17.70				
		323.15	3.704	3.090	19.84				
		348.15	10.60	9.342	13.50				
		373.15	25.22	27.80	−9.28				

of ln *H* versus 1/*T* can be considered in the range of temperatures investigated. Therefore, the temperature dependence of Henry's constants, at a constant pressure, was expressed by

$$\ln H_{ij} = \frac{\Delta H_{\mathrm{dis}\ ij}}{RT} + A_{ij} \qquad (5)$$

where H_{ij}, $\Delta H_{\mathrm{dis}\ ij}$, and A_{ij} are respectively the Henry's constant, the mean enthalpy of dissolution of the solute in the solvent, and a parameter specific for the couple solute (i) − solvent (j); R is the gas constant; and T is the absolute temperature. The values of constants $\Delta H_{\mathrm{dis}\ ij}$ and A_{ij} were determined by linear regressions (appearing as the dotted lines in Figures 3 to 5) with very high correlation coefficients close to 1. They are reported in Table 5.

Predictions with a Thermodynamic Model. Simulations of our vapor−liquid equilibrium results in systems of VOC−phthalate and of the few reported values[2,3] were achieved testing three thermodynamic solution models: UNIQUAC,[6] UNIFAC,[7] and Dortmund modified UNIFAC[8] (UNIFAC DMD) included in the Aspen+ chemical process software. The UNIFAC DMD model, which is known to give the best evaluation of infinite dilution activity coefficients for compounds of very different molecular sizes,[9] appears to be the best one able to fit experimental results and therefore to predict unknown Henry's

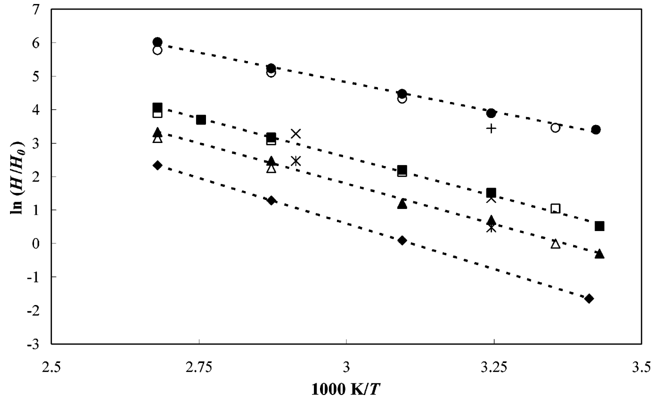

Figure 3. Temperature dependence of ln(H/H_0) (H_0 = 1 kPa, reference unit for H) for couples VOC-DEHP. Toluene: ■, this work; □, ref 2; ×, ref 3. EtB: ▲, this work; △, ref 2; *, ref 3. TMB: ◆, this work. Hexane: ●, this work; ○, ref 2; +, ref 3.

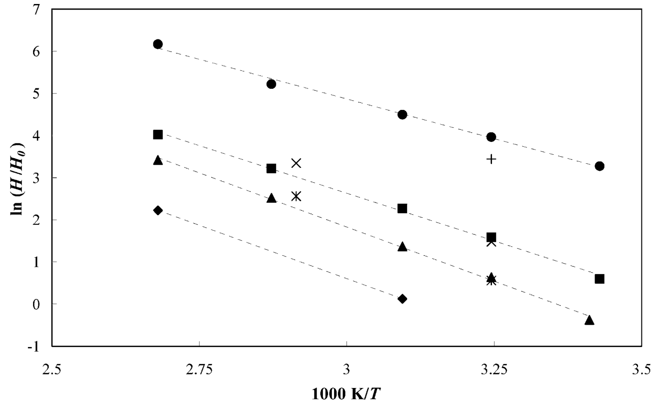

Figure 4. Temperature dependence of ln(H/H_0) (H_0 = 1 kPa, reference unit for H) for couples VOC-DIHP. Toluene: ■, this work; ×, ref 3. EtB: ▲, this work; *, ref 3. TMB: ◆, this work. Hexane: ●, this work; +, ref 3.

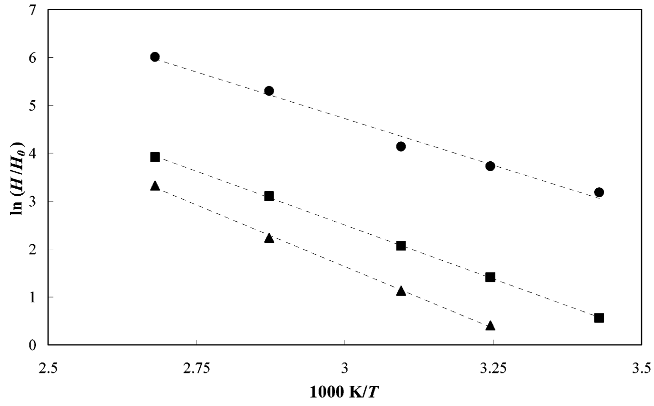

Figure 5. Temperature dependence of ln(H/H_0) (H_0 = 1 kPa, reference unit for H) (experimental results) for ■, toluene; ▲, EtB; and ●, hexane in DINP.

constants. Whereas the models UNIQUAC and UNIFAC provided deviations ranging from (15 to 50) % and (20 to 60) %, respectively, the discrepancy between predicted values obtained by UNIFAC DMD and our experimental results varied from (0 to 30) %, with an average relative deviation of about 11 %. The mean deviation is reduced to 9.4 % if the data obtained at 373.15 K are not taken into account. Measurements of Alessi et al.[2] are predicted with a mean deviation of 7.5 % whereas the mean discrepancy is much higher (27.6 %) for the values of Weisweiler and Winterbauer[3]. Complete results are reported in Table 4.

Table 5. Parameters $\Delta H_{\mathrm{dis}\,ij}$ and A_{ij} of the Temperature Dependence Law of H

phthalate	VOC	$\Delta H_{\mathrm{dis}\,ij}$/(J·mol^{-1})	A_{ij}	R^2
DIHP	hexane	−31356	16.18	0.9945
	toluene	−37618	16.20	0.9971
	EtB	−42777	17.26	0.9981
	TMB	−42027	15.77	1.0000
DEHP	hexane	−29371	15.42	0.9962
	toluene	−38630	16.52	0.9986
	EtB	−40266	16.32	0.9953
	TMB	−45256	16.93	1.0000
DINP	hexane	−32294	16.38	0.9864
	toluene	−37359	15.98	0.9998
	EtB	−42809	17.08	0.9987

Influence of Phthalates on the Solubility of VOC. Computed values by the UNIFAC DMD model presented in Table 4 show that the Henry's constants for all VOC regularly decrease (i.e., the solubilities increase) with increasing molecular weight of the phthalate in the order DIHP, DEHP, DINP. Though not so clearly highlighted by all measured values relative to the three phthalates, due probably to experimental errors and quite similar molecular structures of the phthalates, this tendency is well-revealed comparing DIHP and DINP. This effect was already mentioned by Alessi et al.,[2] who observed a decrease of the activity coefficient γ^∞ for straight-chain and branched-chain phthalates.

Conclusion

Our experimental apparatus and procedure allowed us to determine Henry's constants of four VOC of different volatilities in three heavy phthalates for various temperatures up to 373.15 K. These constants were related to the temperature by linear equations as eq 5 giving the dissolution enthalpies of VOC. Simulations of experimental results with some thermodynamic models confirmed that UNIFAC DMD is the best model to predict Henry's constants for the systems of VOC−phthalate.

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