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Solubility of Hydrogen in the Cyclic Alkylene Ester 1,2-Butylene Carbonate

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The solubility of hydrogen in the cyclic alkylene ester 1,2-butylene carbonate was determined at (283.3, 298.2, and 323.1) K up to a pressure of 9.3 MPa with a high-pressure view-cell technique based on the synthetic method. The solubility of hydrogen in 1,2-butylene carbonate increases with increasing temperature. An extension of Henry's law was employed to correlate the solubility pressures, and the final results for Henry's constant (at zero pressure) of hydrogen in 1,2-butylene carbonate (on the molality scale) are correlated within the experimental uncertainty (about ± 1.4 %) by $\ln(k_{\mathrm{H,H_2}}^{(0)}/\mathrm{MPa}) = 2.123 + 650.96/(T/\mathrm{K})$.

Introduction

The alkylene carbonates or cyclic acid esters are long-term available solvents that are primarily used as degreasers and paint strippers.[1,2] A major aspect of what today is called "Green Chemistry", i.e., to adapt industrial processes to environmental needs while maintaining or even improving performance and economic viability, targets the role of solvents. Research is looking for alternatives to the noxious volatile organic compounds (VOCs), traditionally standard media for industrial synthesis. Many of these solvents are toxic, flammable, nondegradable, difficult to recycle, and released into the environment in enormous quantities. In recent years, two "unusual" materials have become established at the forefront of conventional solvent replacement, supercritical fluids, primarily supercritical carbon dioxide, and ionic liquids.[3] Supercritical fluids are hybrids of liquid and gas, and ionic liquids are salts that are liquid at ambient temperature. As alkylene carbonates exhibit low volatility, low toxicity, and biodegradability combined with excellent solvency properties for many organic and inorganic materials,[1] attention is drawn to that class of solvents as well. For the past few years, alkylene carbonates gain considerable interest and enter further applications in addition to their use as inert media. Alkylene carbonates find increasing utility as reactive intermediates (e.g., they react with amines, alcohols, carboxylic acids, etc.), and they are the standard electrolyte in lithium ion batteries.[1]

Not surprisingly, the quest for alternative solvents will account and also compare the properties of alkylene carbonates and ionic liquids to find out the best performing candidate. The electrolyte systems for lithium ion batteries[4−6] are applications where alkylene carbonates compete with ionic liquids. Both kinds of solvents can equally provide a wide electrochemical window as well as good chemical stability. Ionic liquids have some advantages over alkylene carbonates; for example, they are nonflammable, and due to their ionic nature, their electrochemical properties can be tailored in two ways. First, the molecular structure can be adapted by modifying a cation or anion, and second, cations and anions themselves can be combined intentionally.

Ionic liquids are well established in the field of transition-metal catalysis. To pick just two applications out of many more, ionic liquids are successfully applied in biphasic hydrogenation and hydroformylation.[7] To describe it briefly, in such a biphasic reaction mode, there are two mutually immiscible liquids, but they must still allow sufficient interphase mass transfer to keep the reaction going. The transition metal complex is immobilized (and therefore recyclable) in one (i.e., the ionic liquid) phase, and the product is an important constituent of the second phase (see, for example, Keim[8]). One of the most beneficial ionic liquid properties is the extremely low vapor pressure that simplifies the treatment of volatile products or other reaction agents considerably. However, alkylene carbonates have also come under closer inspection as a potential polar and aprotic solvent for transition metal catalysis.

Recently, the group of Börner at the University of Rostock published a paper on propylene carbonate as a solvent for asymmetric hydrogenation (Bayardon et al.[9]). By comparing propylene carbonate with methanol, tetrahydrofurane, or methylene chloride, an—at least similar but normally even enhanced—enantioselectivity was found that could be increased by increasing the pressure. Bayardon et al.[9] showed that the reaction products can be extracted with a nonpolar solvent (e.g., hexane), while the catalyst exclusively remained in the propylene carbonate phase. Behr et al. reported a selective transition-metal catalyzed hydroformylation of *trans*-4-octene to *n*-nonanal by application of a so-called temperature-dependent multicomponent solvent system.[10] There, three solvents of different polarity are employed. The first solvent contains the catalyst, and the second solvent must be largely immiscible with the first solvent but extracts the reaction product. The third solvent (also called mediator) is of medium polarity, so that a ternary mixture of the three solvents can change from a homogeneous to a heterogeneous state when the temperature is changed. The reaction can thus be executed in a homogeneous phase, and usually by lowering the temperature, the catalyst phase can be separated from the product phase. At separation temperature, the mediator and the alkylene carbonate should be immiscible with the extraction agent to suppress catalyst leaching into the product phase. Behr et al. investigated several alkylene carbonates as the catalyst-containing phase.

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Table 1. Density of 1,2-Butylene Carbonate (Estimated Experimental Uncertainty: $\Delta\rho = \pm\ 0.0001\ \mathrm{kg \cdot dm^{-3}}$)

T/K	$\rho/(\mathrm{kg \cdot dm^{-3}})$
283.0	1.1552
293.1	1.1466
295.1	1.1449
297.1	1.1433
299.1	1.1417
301.1	1.1401
303.1	1.1386

These two examples show that an alkylene carbonate shares some characteristics with an ionic liquid, for example, low volatility and the capability to stabilize the catalyst. Drawbacks for the ionic liquid in this assessment, however, are high material costs and less biodegradability. Since alkylene carbonates (still) are substantially cheaper than ionic liquids, they are considered as an alternative (an economically favorable) solvent in transition metal catalysis. The solubility behavior of the reaction gas in that phase where the reaction takes place is a key question for development and design of such processes.

In this paper, we present experimental data for the solubility of hydrogen in 1,2-butylene carbonate at (283.3, 298.2, and 323.1) K up to a maximum pressure of about 10 MPa.

Experimental Section and Results

Apparatus and Method. We employed the same apparatus and the corresponding measuring technique as reported previously for the investigation of gas solubilities in ionic liquids.[11,12] For a detailed outline, particularly for experiments with hydrogen, the reader is referred to previous publications[11−14] and the references cited therein.

The mass of hydrogen introduced into the cell was determined volumetrically, i.e., from the known volume of the cell (approximately 29.1 cm^3) and readings for temperature and pressure via the virial equation of state which was truncated after the second virial coefficient.[15] The operational temperature was measured using two calibrated platinum resistance thermometers with an uncertainty of less than ± 0.1 K. When the cell was charged with hydrogen, the pressure was measured with two pressure transducers suitable for a maximum pressure of (0.25 and 0.6) MPa, respectively. The amount of mass of 1,2-butylene carbonate solvent filled into the cell (about 33 g) was calculated from the volume displacement in a calibrated spindle press, from which the solvent was pumped into the gas-filled cell, and the solvent density. The solvent density was separately determined with a vibrating tube densimeter (DMA 602, Anton Paar GmbH, Graz, Austria) in the temperature region between (283.0 and 303.1) K. The results are given in Table 1. They can be correlated by

$$\rho/(\mathrm{kg \cdot dm^{-3}}) = 1.65833 - 0.0026667(T/\mathrm{K}) + 3.141 \cdot 10^{-6}(T/\mathrm{K})^2 \quad (1)$$

The solubility pressure was measured with two pressure transducers suitable up to (2.5 and 10) MPa. All pressure transducers were from WIKA GmbH, Klingenberg, Germany, and calibrated against a high-precision pressure balance (Desgranges & Huot, Aubervilliers, France) before and after each measurement series. The maximum systematic uncertainty in the solubility pressure measurement results from the intrinsic uncertainty of the pressure transducers (i.e., 0.1 % of the transducer's full scale) and an additional contribution of about ± 0.02 MPa from small temperature fluctuations of the isolated (high-pressure) tubes filled with the solvent that connect the view-cell with the pressure transducers.

Table 2. Experimental Results for the Solubility of Hydrogen in 1,2-Butylene Carbonate

T	m_{H_2}	p	f_{H_2}/m_{H_2}	$V_{cell}/\tilde{m}_{solv}$
K	$(\mathrm{mol \cdot kg^{-1}})$	MPa	MPa/$(\mathrm{mol \cdot kg^{-1}})$	$(\mathrm{cm^3 \cdot kg^{-1}})$
283.3 ± 0.1	0.01765 ± 0.00011	1.472 ± 0.031	84.1 ± 1.4	866.3 ± 2.7
	0.02997 ± 0.00013	2.509 ± 0.041	84.9 ± 1.1	866.9 ± 2.7
	0.04624 ± 0.00017	3.921 ± 0.044	86.7 ± 0.7	865.4 ± 2.7
	0.05951 ± 0.00021	4.993 ± 0.047	86.4 ± 0.6	866.1 ± 2.7
	0.07350 ± 0.00025	6.219 ± 0.051	87.7 ± 0.5	866.3 ± 2.7
	0.08998 ± 0.00030	7.637 ± 0.055	88.7 ± 0.4	865.2 ± 2.7
	0.10677 ± 0.00058	9.120 ± 0.078	90.0 ± 0.6	865.4 ± 2.7
298.2 ± 0.1	0.02995 ± 0.00013	2.235 ± 0.032	75.6 ± 0.8	877.5 ± 2.8
	0.04416 ± 0.00017	3.299 ± 0.042	76.1 ± 0.7	877.6 ± 2.8
	0.06023 ± 0.00021	4.524 ± 0.046	77.0 ± 0.6	877.6 ± 2.8
	0.07141 ± 0.00024	5.379 ± 0.048	77.6 ± 0.5	876.7 ± 2.8
	0.08962 ± 0.00030	6.784 ± 0.052	78.6 ± 0.4	876.5 ± 2.8
	0.10654 ± 0.00040	8.061 ± 0.060	79.2 ± 0.4	876.4 ± 2.8
	0.12101 ± 0.00044	9.179 ± 0.062	79.8 ± 0.4	876.5 ± 2.8
323.1 ± 0.1	0.02521 ± 0.00012	1.582 ± 0.030	63.3 ± 0.9	895.8 ± 2.8
	0.04691 ± 0.00017	2.955 ± 0.041	64.0 ± 0.7	895.9 ± 2.8
	0.06665 ± 0.00023	4.228 ± 0.044	64.9 ± 0.5	894.6 ± 2.8
	0.08557 ± 0.00034	5.440 ± 0.051	65.4 ± 0.4	895.0 ± 2.8
	0.10562 ± 0.00039	6.716 ± 0.054	65.9 ± 0.4	895.3 ± 2.8
	0.12554 ± 0.00045	8.008 ± 0.058	66.6 ± 0.3	894.4 ± 2.8
	0.14535 ± 0.00050	9.269 ± 0.061	67.0 ± 0.3	895.5 ± 2.8

Materials and Sample Pretreatment. Hydrogen (mole fraction ≥ 0.99999) was purchased from Messer Griesheim GmbH, Ludwigshafen, Germany, and used without further purification. 1,2-Butylene carbonate (4-ethyl-1,3-dioxolan-2-one, $C_5H_8O_3$, CAS-No. 4437-85-8, JEFFSOL grade, mass fraction > 0.9999, colorless liquid, relative molar mass $M = 116.12$) was from Huntsman Petrochemical Co., Conroe, TX, USA. The samples were introduced into a glass buret so that they could be handled and transferred into the apparatus under vacuum. Initially, the buret was connected to a vacuum pump for drying and degassing. Vacuum conditions and a frequent vigorous shaking of the buret during a period of half an hour proved sufficient. Each solubility measurement was performed with a fresh sample. Neither the color nor the odor of 1,2-butylene carbonate was affected by the measurement.

Experimental Results. The solubility of hydrogen in 1,2-butylene carbonate was investigated at (283.3, 298.2, and 323.1) K up to approximately 10 MPa. The new experimental results and the corresponding experimental uncertainties are given in Table 2. There, the pressure p (i.e., the so-called solubility pressure) is the pressure required to dissolve a certain amount of hydrogen in 1 kg of 1,2-butylene carbonate at a definite temperature. The corresponding gas molality m_{H_2} is the amount of substance (the number of moles) of the gas that is absorbed by 1 kg of 1,2-butylene carbonate at that temperature. Figure 1 shows the solubility isotherms as pressure p plotted versus gas molality m_{H_2}.

Within the temperature and pressure regions investigated during this study, the solubility pressure monotonously increases with increasing gas molality at a constant temperature. In accordance with the behavior of gases that exhibit extremely low absolute solubility, the solubility (or the gas molality) increases with increasing temperature at a constant pressure. Figure 1 also shows that the solubility isotherms almost run linearly. These observations are characteristic for a purely physical solubility behavior. For example, at $p = 6$ MPa, about 0.070 (0.093) moles of hydrogen dissolve in 1 kg of 1,2-butylene carbonate at 283.3 K (323.1 K). In a solubility experiment, the state of equilibrium was accomplished after at minimum of one hour for all temperatures.

The experimental absolute (relative) uncertainty for the gas molality Δm_{H_2} $(\Delta m_{H_2}/m_{H_2})$ caused by the filling procedure was

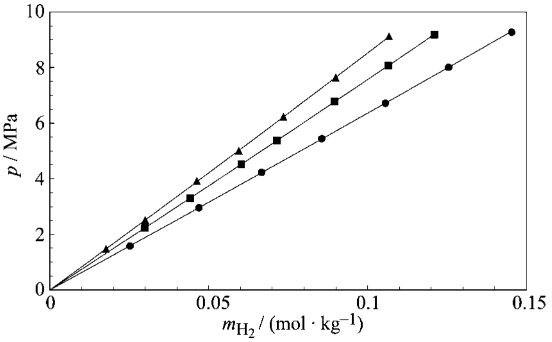

Figure 1. Total pressure above solutions of (hydrogen + 1,2-butylene carbonate): ▲, 283.3 K; ■, 298.2 K; ●, 323.1 K experimental results; −, correlation.

estimated from a Gauss error propagation calculation and amounts at average to 0.00028 mol·kg^{-1} (0.4 %). The experimental uncertainty for the solubility pressure p was calculated from $\Delta p = \pm (\Delta p_{sys} + \Delta p_{stat})$. The first term accounts for the systematic uncertainties (i.e., pressure transducer's uncertainty (0.1 % of the transducer's full scale) + uncertainty resulting from the temperature drift (0.02 MPa)). The second term is a statistical one from a Gauss error propagation calculation (by applying the VLE model described in the next section). It reflects the effect of the uncertainties of temperature and gas molality on the solubility pressure p. The absolute (relative) uncertainty in the pressure Δp ($\Delta p/p$) amounts in average to 0.049 MPa (1.1 %) for the system investigated. The relative uncertainty decreases from (at maximum) 2.1 % at low pressures to (at minimum) 0.7 % at the highest pressures.

Correlation of Gas Solubility. The correlation method applied here is to a great extent similar to the method that was applied for the correlation of hydrogen solubilities in ionic liquids.[12−14] If one assumes that the vapor pressure of 1,2-butylene carbonate at the investigated temperatures is negligibly small (in the same way as common for ionic liquids, since, according to Verevkin et al.,[16] at 323.1 K, 1,2-butylene carbonate has a vapor pressure p^{sat} = 29.85 Pa), the gaseous phase consists of pure hydrogen. Thus, the vapor−liquid equilibrium condition is only applied to the gaseous component and results in the extended Henry's law

$$k_{H,H_2}(T,p)\, a_{H_2}(T, m_{H_2}) = f_{H_2}(T,p) \tag{2}$$

$k_{H,H_2}(T, p)$ is Henry's constant of hydrogen in liquid 1,2-butylene carbonate at temperature T and pressure p (based on the molality scale). $a_{H_2}(T,m_{H_2})$ is the activity of the gas in the liquid, and the influence of pressure on that activity is neglected. $f_{H_2}(T,p)$ is the fugacity of hydrogen in the vapor phase.

The Henry's constant of hydrogen in 1,2-butylene carbonate is expressed as

$$k_{H,H_2}(T,p) = k^{(0)}_{H,H_2}(T) \exp\left(\frac{V^{(\infty)}_{m,H_2} p}{RT}\right) \tag{3}$$

where $k^{(0)}_{H,H_2}(T)$ is Henry's constant at zero pressure; $V^{(\infty)}_{m,H_2}$ is the partial molar volume at infinite dilution of hydrogen in 1,2-butylene carbonate; and R is the universal gas constant.

The hydrogen activity in 1,2-butylene carbonate (on the molality scale) is defined as

$$a_{H_2} = \frac{m_{H_2}}{m^\circ} \gamma_{H_2} \tag{4}$$

where m° = 1 mol·kg^{-1}. Due to the very low solubility of hydrogen, the liquid mixture can be considered as an ideal solution,[12−14] i.e., the activity coefficient $\gamma_{H_2} = 1$.

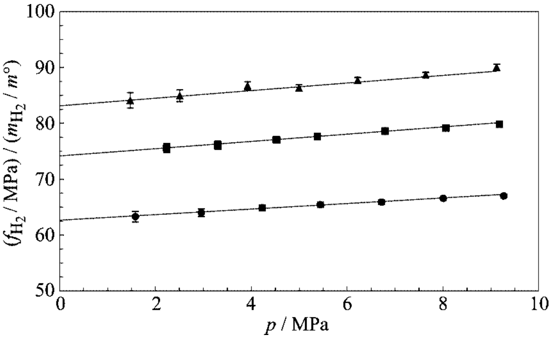

Figure 2. Evaluation of the experimental results for the solubility of hydrogen in 1,2-butylene carbonate to determine Henry's constant: ▲, 283.3 K; ■, 298.2 K; ●, 323.1 K experimental results (and estimated uncertainties); −, linear fit.

The fugacity of hydrogen f_{H_2} at equilibrium temperature and pressure is the product of the total pressure p and the fugacity coefficient $\phi_{H_2}(T,p)$

$$f_{H_2}(T,p) = p\phi_{H_2}(T,p) \tag{5}$$

The virial equation of state, truncated after the second virial coefficient, was employed to calculate the fugacity coefficients $\phi_{H_2}(T,p)$

$$\phi_{H_2}(T,p) = \exp\left[\frac{B_{H_2,H_2} p}{RT}\right] \tag{6}$$

The second virial coefficient of hydrogen B_{H_2,H_2} was calculated from a correlation which is based on experimental data recommended by Hayden and O'Connell[15]

$$\frac{B_{H_2,H_2}}{\text{cm}^3 \cdot \text{mol}^{-1}} = 17.674 - 63.844\left(\frac{43.6}{T/\text{K}}\right)^{1.467} \tag{7}$$

In the temperature range investigated, the second virial coefficient of hydrogen stretches from 13.57 cm^3·mol^{-1} at 283.3 K to 14.29 cm^3·mol^{-1} at 323.1 K, and the fugacity coefficient of hydrogen is slightly above one (5.4 % at maximum).

Henry's constant of hydrogen in 1,2-butylene carbonate at zero pressure $k^{(0)}_{H,H_2}(T)$ was determined by an extrapolation (at fixed temperature) of the experimental results for the solubility pressure

$$k^{(0)}_{H,H_2}(T) = \lim_{p\to 0}\left[\frac{f_{H_2}(T,p)}{(m_{H_2}/m^\circ)}\right] \tag{8}$$

Figure 2 shows an isothermal plot of $f_{H_2}/(m_{H_2}/m^\circ)$ versus the solubility pressure. The results for $f_{H_2}/(m_{H_2}/m^\circ)$ with the estimated uncertainties from a Gauss error propagation calculation are also given in Table 2. A linear regression proved sufficient to determine $k^{(0)}_{H,H_2}(T)$. The number of experimental data points used in the extrapolation process should have no influence on the final result for Henry's constant as long as that number of experimental data points is sufficiently large. Therefore, the extrapolation was repeated omitting randomly selected single or double data points. The given uncertainty is the deviation between the optimum value (i.e., the result from all data points included) and the results from all these evaluations (i.e., with one or two data points omitted). Table 3 lists the numerical values for Henry's constant (at zero pressure and on the molality scale) from this procedure.

The estimated relative uncertainty for those Henry's constants amounts in average to 1.4 %, and a linear function satisfactorily correlates Henry's constant (at zero pressure and on the molality scale) as a function of temperature within the estimated uncertainty

$$\ln(k^{(0)}_{\mathrm{H,H_2}}/\mathrm{MPa}) = 2.123 + 650.96/(T/\mathrm{K}) \qquad (9)$$

Figure 3 shows that Henry's constant decreases with increasing temperature, and the same behavior was observed during the experiments of hydrogen solubility in some ionic liquids.[12−14]

The correlation of the solubility pressure, i.e., the curves displayed in Figure 1, resorts to eqs 2 to 4. The assumed ideal mixing behavior implicates $\gamma_{\mathrm{H_2}} = 1$, so that the partial molar volume at infinite dilution of hydrogen in 1,2-butylene carbonate $V^{(\infty)}_{\mathrm{m,H_2}}$ remains the only unknown property. Basically, the partial molar volume at infinite dilution can be determined by our experimental technique as well. We explain in another paper how to evaluate that quantity and discuss its relevance for the calculation of solution thermodynamic properties.[17] Hydrogen is poorly soluble in 1,2-butylene carbonate, and a good agreement between experimental and correlated solubility pressures was already accomplished with $V^{(\infty)}_{\mathrm{m,H_2}}$ = const. The maximum absolute (relative) deviation from a calculation that employed $V^{(\infty)}_{\mathrm{m,H_2}} = 20.3\ \mathrm{cm^3 \cdot mol^{-1}}$ does not exceed 0.033 MPa (0.8 %). The uncertainty of the partial molar volume of hydrogen in 1,2-butylene carbonate from such an evaluation was estimated as described previously:[17] $\Delta V^{(\infty)}_{\mathrm{m,H_2}} \approx 10\ \mathrm{cm^3 \cdot mol^{-1}}$. Figure 4 shows a plot $(V_{\mathrm{cell}}/\tilde{m}_{\mathrm{solv}})$ versus the equilibrium gas molality $m_{\mathrm{H_2}}$ at a constant temperature, and the corresponding data are given in Table 2. The experimental uncertainty for the property $(V_{\mathrm{cell}}/\tilde{m}_{\mathrm{solv}})$ is also estimated from a Gauss error propagation calculation. The slope of the linear functions in Figure 4 represents the partial molar volume at infinite dilution $V^{(\infty)}_{\mathrm{m,H_2}}$ of hydrogen in 1,2-butylene carbonate.[17] The functions at (283.3 and 298.2) K were anchored in the independently measured specific volume of pure 1,2-butylene carbonate on the ordinate in Figure 4 (cf. eq 1), whereas for 323.1 K that value was determined by extrapolation to zero gas molality from the best fit to the volumetric data from the gas solubility measurements and results in $894.0\ \mathrm{cm^3 \cdot kg^{-1}}$ (that corresponds to $\rho = 1.1186\ \mathrm{kg \cdot dm^{-3}}$). Because $V^{(\infty)}_{\mathrm{m,H_2}}$ = const., all three linear functions are parallel, and they run within the experimental uncertainty of the $(V_{\mathrm{cell}}/\tilde{m}_{\mathrm{solv}})$ values. That plot, however, also shows that a reliable evaluation of the volumetric data is not possible (as recently shown for other (gas + poor solvent) systems).[17]

(Molar) solution properties $\Delta_{\mathrm{sol}}X^{\mathrm{o}}_{\mathrm{m}}$, where, for example, X can be replaced by G (i.e., the Gibbs energy), H (i.e., the enthalpy), or S (i.e., the entropy), can be calculated from Henry's constant $k_{\mathrm{H,H_2}}(T, p)$. At standard conditions ($T^{\circ} = 298.15$ K, $p^{\circ} = 0.1$ MPa) and on the molality scale, the following properties result

$$\Delta_{\mathrm{sol}}G^{\mathrm{o}}_{\mathrm{m}} = (16.385 \pm 0.034)\ \mathrm{kJ \cdot mol^{-1}}$$

$$\Delta_{\mathrm{sol}}H^{\mathrm{o}}_{\mathrm{m}} = (5.41 \pm 0.25)\ \mathrm{kJ \cdot mol^{-1}}$$

$$\Delta_{\mathrm{sol}}S^{\mathrm{o}}_{\mathrm{m}} = (-36.80 \pm 0.85)\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$$

Comparison with Literature Data

The correlations for Henry's constant (at zero pressure and on the molality scale) of hydrogen in the three previously investigated ionic liquids, [bmim][PF_6],[14] [bmim][CH_3SO_4],[12] and [hmim][Tf_2N],[13] allow us to compare the results for the solubility of hydrogen in 1,2-butylene carbonate with the results from those studies. The Henry's constant of hydrogen in 1,2-butylene carbonate is lower than Henry's constant of hydrogen in each of the ionic liquids, which means that 1,2-butylene carbonate can absorb more hydrogen than [bmim][PF_6], [bmim][CH_3SO_4], or [hmim][Tf_2N] in the p,T region investigated. The corresponding values (cf. Table 3) illustrate this difference. At $T = 283.3$ K, Henry's constants for hydrogen in [bmim][PF_6], [bmim][CH_3SO_4], and [hmim][Tf_2N] differ from the corresponding value for hydrogen in 1,2-butylene carbonate by a factor of 1.73, 2.18, and 1.10, respectively. The divergence slightly increases toward higher temperatures, and this factor becomes 1.77, 2.22, and 1.18, respectively, at $T = 323.1$ K.

The homologous cyclic ester propylene carbonate, however, has already been subject to investigations of hydrogen solubility at comparable (p,T) conditions. For comparison, the original solubility data were transformed into molality scale units (cf. Appendix) and—as far as possible—evaluated for Henry's constant at zero pressure.

In 1966, Schmack and Bittrich determined the solubility between (278.15 and 333.15) K in 5 K intervals at pressures of (1 and 10) atm, respectively.[18] The comparison with the new gas solubility data reveals that 1,2-butylene carbonate is a better solvent for hydrogen than propylene carbonate. For example, at 283.15 K and 10 atm (at 323.15 K and 1 atm), the solubility is higher by about 4 % (12 %). But, according to Schmack and Bittrich, the solubility of hydrogen in propylene carbonate at 323.15 K and 10 atm is about 2 % above the corresponding data from the present investigation for the solubility of hydrogen in 1,2-butylene carbonate. However, these differences have to be considered in view of an uncertainty of 8 % that was estimated by Schmack and Bittrich for their experimental results.[18]

Shakhova et al. also reported experimental results for the solubility of hydrogen in propylene carbonate at the same temperatures as in the present study but at elevated pressures between about (7 and 14) MPa.[19] As shown in Figure 5, these results again indicate a lower solubility in propylene carbonate than in 1,2-butylene carbonate. The average relative deviation between these results (molalities at p,T) in propylene carbonate and the results from the present work amounts to about 30 %; Shakhova et al. estimated the experimental uncertainty to be 5 %. However, there is a rather large scattering within an isotherm. Nevertheless, the data were evaluated to determine Henry's constant of hydrogen in propylene carbonate at zero pressure $k^{(0)}_{\mathrm{H,H_2}}(T)$ employing eq 8. The results are given in Table 3.

Table 3. Comparison of Henry's Constant of Hydrogen in 1,2-Butylene Carbonate, Propylene Carbonate, and the Ionic Liquids [bmim][PF_6], [bmim][CH_3SO_4], and [hmim][Tf_2N] at Zero Pressure and on the Molality Scale

	$k^{(0)}_{\mathrm{H,H_2}}$/MPa				
substance	T/K = 283.3	T/K = 298.2	T/K = 323.1	T/K = 398.15	source
1,2-butylene carbonate	83.1 ± 1.3	74.2 ± 0.9	62.7 ± 0.9	—	this work, experiment
	83.16	74.14	62.66	42.86	this work, correlation (eq 9)
propylene carbonate	120 ± 25	112 ± 15	85 ± 13	—	ref 19, calculated from experimental data
	—	92.3	90.2	55.8	ref 20
[bmim][PF_6]	143.46	129.25	110.93	78.56	ref 14, correlation
[bmim][CH_3SO_4]	181.08	162.84	139.38	98.10	ref 12, correlation
[hmim][Tf_2N]	91.33	83.74	73.74	55.34	ref 13, correlation

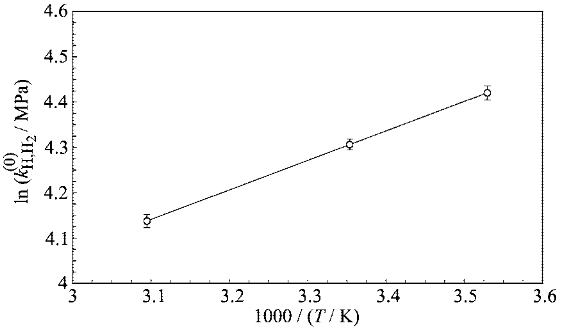

Figure 3. Henry's constant of hydrogen in 1,2-butylene carbonate (at zero pressure, on the molality scale): ○, extrapolated experimental results (and estimated uncertainties); −, correlation.

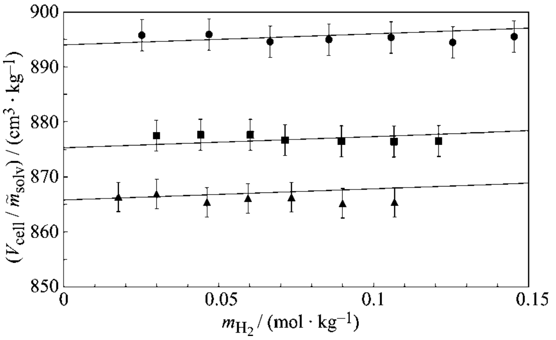

Figure 4. Volumetric data from the investigations of the system (hydrogen + 1,2-butylene carbonate): ▲, 283.3 K; ■, 298.2 K; ●, 323.1 K experimental results (and estimated uncertainties); −, linear function with $V^{(\infty)}_{\mathrm{m,H_2}} = 20.3$ cm^3·mol^{-1}.

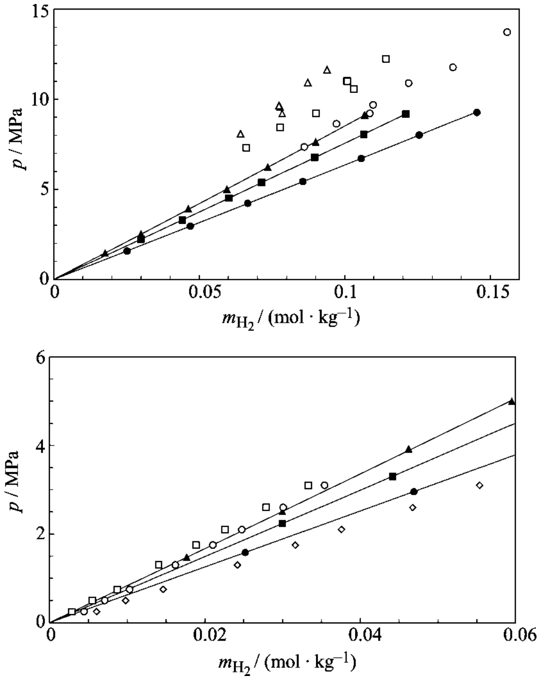

Figure 5. Total pressure above solutions of (hydrogen + solvent). Solvent: 1,2-butylene carbonate: ▲, 283.3 K; ■, 298.2 K; ●, 323.1 K experimental results; −, correlation. Solvent: propylene carbonate: experimental results by Shakhova et al.:[18] Δ, 283.15 K; □, 298.15 K; ○, 323.15 K (top); experimental results by Obst:[20] □, 298.15 K; ○, 323.15 K; ◇, 398.15 K (bottom).

Recently, Behr et al.[20] published a paper on the reaction kinetics for the hydroformylation of *trans*-4-octene that was elaborated from the doctoral thesis of Obst.[21] Prior to the kinetic studies, the solubility of hydrogen in propylene carbonate was determined at (298.15, 323.15, and 398.15) K, respectively, up to a maximum pressure of 3.1 MPa. These results agree with those reported in the other studies. The original solubility data are also shown in Figure 5.

Since Behr et al. did not give any details on the experimental uncertainty of the gas solubility data,[20] the corresponding Henry's constants in Table 3 are the original values taken from the paper and only transformed into the molality scale. To give an example for the solubility difference, at 298.15 K (323.15 K) and 2.6 MPa, the solubility of hydrogen in 1,2-butylene carbonate measured in the present work is about 19 % (26 %) higher compared with the results for propylene carbonate.

Conclusions

New experimental results for the solubility of hydrogen in 1,2-butylene carbonate at (283.3, 298.2, and 323.1) K up to a pressure of 9.3 MPa are reported and evaluated by means of an extension of Henry's law. The solubility of hydrogen in 1,2-butylene carbonate increases with rising temperature, which is typical for a poorly soluble gas. The gas molality is as low as 0.145 kg·mol^{-1} at 323.1 K and 9.27 MPa. A literature survey revealed that the solubility of hydrogen in 1,2-butylene carbonate is considerably higher than in related solvents such as propylene carbonate or imidazolium-based room-temperature ionic liquids, i.e., solvents that are currently discussed as reaction media for hydroformylation reactions. Reaction engineering might profit from that rather astonishing phenomenon since in hydroformylation carbon monoxide and hydrogen are reactants and thus gas solubility is an important factor.

Appendix

Transformation of Literature Gas Solubility Data to the Molality Scale.

In elder literature, gas solubility is often given as the dimensionless "Bunsen absorption coefficient". For the sake of better clarity, the equations are given which were employed to transform these data to the molality scale. The Bunsen coefficient α is defined as the volume of the dissolved gas (reduced to $t° = 0$ °C and $p° = 1$ atm) that is absorbed by a unit volume of pure solvent at the temperature of measurement and partial pressure $p° = 1$ atm (1 atm = 0.101325 MPa)

$$\alpha = \frac{V_{\mathrm{gas}}(t°, p°)}{V^{*}_{\mathrm{liq}}(t)} \tag{10}$$

The mole fraction solubility x_{gas} is expressed as

$$x_{\mathrm{gas}} = \frac{1}{1 + \dfrac{\rho_{\mathrm{liq}}(T)}{\alpha M_{\mathrm{liq}}} \cdot \dfrac{RT°}{p°}} = \frac{1}{1 + \dfrac{\rho_{\mathrm{liq}}(T)}{\alpha M_{\mathrm{liq}}} \cdot 22414} \tag{11}$$

In eq 11, the factor of 22 414 ensues from $\rho_{\mathrm{liq}}(T)$ given in the unit g·cm^{-3} and M_{liq} in g·mol^{-1}. $R = 8.3145$ J·mol^{-1}·K^{-1}, $T° = 273.15$ K, and $p° = 101325$ N·m^{-2}. The gas molality m_{gas} is calculated from the mole fraction solubility x_{gas} via

$$\frac{m_{\mathrm{gas}}}{m°} = \frac{x_{\mathrm{gas}}}{x_{\mathrm{liq}} M^{*}_{\mathrm{liq}}} \tag{12}$$

where $M^{*}_{\mathrm{liq}} = M_{\mathrm{liq}}/1000$ (here, M_{liq} is the relative molar mass) and $m° = 1$ mol·kg^{-1}.

Table 4 lists the original solubility data together with the resulting gas molality by employing eqs 11 and 12. In all probability, however, the given α at $p \neq 1$ atm from the paper

Table 4. Literature Data of Experimental Results for the Solubility of Hydrogen in Propylene Carbonate

t / °C	p / atm	α	ρ_{liq} / $(kg \cdot dm^{-3})^a$	m_{H_2} / $(mol \cdot kg^{-1})$	source
10	1	0.0290	1.2166	0.00106	ref 18
	10	0.0312		0.01144	
25	1	0.0320	1.1996	0.00119	
	10	0.0342		0.01272	
50	1	0.0368	1.1714	0.00140	
	10	0.0427		0.01626	
	p^b / at	α			
10	82.3	1.75	1.2166	0.06418	ref 19
	93.9	2.14		0.07848	
	97.6	2.12		0.07775	
	98.3	2.11		0.07738	
	111.4	2.38		0.08728	
	118.6	2.56		0.09388	
25	74.6	1.78	1.1996	0.06620	
	86.2	2.09		0.07773	
	93.9	2.42		0.09000	
	107.9	2.77		0.10302	
	112.3	2.71		0.10079	
	124.9	3.07		0.11418	
50	75.0	2.26	1.1714	0.08608	
	88.1	2.55		0.09712	
	93.9	2.85		0.10855	
	98.8	2.88		0.10969	
	111.1	3.20		0.12188	
	120.0	3.60		0.13711	
	139.9	4.09		0.15578	
T / K	p / MPa		x_{H_2} / $(mol \cdot mol^{-1})$		
298.15	0.25		0.00029	0.00284	ref 21
	0.5		0.00056	0.00551	
	0.75		0.00089	0.00870	
	1.3		0.00143	0.01403	
	1.75		0.00192	0.01884	
	2.1		0.00230	0.02258	
	2.6		0.00284	0.02790	
	3.1		0.00339	0.03332	
323.15	0.25		0.00045	0.00444	
	0.5		0.00072	0.00710	
	0.75		0.00105	0.01030	
	1.3		0.00165	0.01619	
	1.75		0.00214	0.02101	
	2.1		0.00252	0.02475	
	2.6		0.00306	0.03007	
	3.1		0.00360	0.03539	
398.15	0.25		0.00062	0.00604	
	0.5		0.00100	0.00977	
	0.75		0.00149	0.01462	
	1.3		0.00246	0.02416	
	1.75		0.00322	0.03164	
	2.1		0.00382	0.03756	
	2.6		0.00475	0.04675	
	3.1		0.00562	0.05536	

[a] According to eq 14. [b] 1 at = 0.098066 MPa.

by Schmack and Bittrich[18] is to be transformed by applying a slightly modified equation

$$x_{gas} = \frac{1}{1+\frac{\rho_{liq}(T)}{\alpha M_{liq}}\cdot\frac{RT^\circ}{p}} = \frac{1}{1+\frac{\rho_{liq}(T)}{\alpha M_{liq}}\cdot\frac{p^\circ}{p}\cdot 22414} \qquad (13)$$

The density ρ_{liq} (T) of propylene carbonate was calculated using a correlation function that is based on data from various publications[22−27]

$$\rho/(kg \cdot dm^{-3}) = 1.53627 - 0.0011291(T/K) \qquad (14)$$

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