

Studies on Self-diffusion of Main Components of Hop Oils

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The self-diffusion coefficients (D) of α -humulene and myrcene, which are main components of hop oils, were measured at the temperature range of 274–372 K and pressures up to 100 MPa by the Stejskal-Tanner FT NMR method. In order to obtain motional behavior of the molecules in the supercritical conditions, the intradiffusion coefficients (D_{ii}) of the two substances in carbon dioxide were also determined. It was found that the values of D_{ii} are about one order of magnitude higher than that for the pure components at the same ranges of temperature and pressure. The self-diffusion data of α -humulene and myrcene are analysed, and the diffusion behavior of these compounds is discussed.

Keywords Hop oil, supercritical carbon dioxide, self-diffusion coefficient, NMR

Introduction

The self-resp. intradiffusion coefficient D is a basic property which characterizes quantitatively translational motion of molecules in liquids. In previous work we reported the temperature and pressure dependence of diffusion in neat fluids¹⁻³ and in fluid solutions containing CO₂ or ammonia.⁴

CO₂ is commonly applied supercritical fluid in industrial processes. The supercritical CO₂ is widely used as solvent for extraction or refining of products in agriculture, food and pharmaceutical industries, *etc.*, as well as a good medium for a great variety of reactions.^{5,6} For the optimization of these extraction processes it is necessary to provide knowledge of the dynamic behaviors such as the diffusion and viscosity data, and their temperature and pressure dependence. A quantitative description of the density and pressure dependence of the

transport properties for the fluid state may be possible only after the collection of experimental data of the dynamics.

The extraction of valuable components from hops using CO₂ as extraction solvent is one of the earliest commercial productions applying the supercritical fluid techniques. There are two techniques for the extraction of hop oils: (1) The production was undertaken on the condition of about 281 K and 6×10^6 Pa. In this process the hop oils were selectively extracted from the raw material by liquid CO₂, and their main components are the soft resins and ethereal oils; (2) The extraction was carried out at the temperature range of 313–333 K and pressures up to 3.5×10^7 Pa with the supercritical CO₂. Under this condition, the products are olive green oils having a rich fragrance. The main components of hop oils produced by the HVG Barth Raiser & Co. (Wolnzach, Germany) using the supercritical CO₂ extraction process are α -humulene (21%), myrcene (42%) and β -caryophyllene (18%).

In order to provide some data for the design of extraction equipments and to understand the mass transport processes in the supercritical conditions, in this paper we report the results on self-diffusion of α -humulene and myrcene as well as in mixtures containing CO₂.

Experimental

Substances

The compounds were of commercial quality and used without further purification: α -Humulene > 98% (Fluka Co., Buchs, Switzerland); Myrcene 81%—

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92% (Roth Co., Karlsruhe, Germany); CO₂ 99.995% (AGA-Gas, Hamburg, Germany).

The proton NMR spectra of these solutes at a S/N ratio of > 100 does not show any additional signals. CO₂ was directly pressed into the high pressure separation volume. The mixtures were prepared by weighing.

Diffusion measurements

The diffusion measurement is a good method for probing the molecular dynamics in the fluid state. At present, the NMR Hahn Spin-echo technique with application of pulsed field gradients has become the method of choice.⁷ The self-diffusion coefficient D is determined by measuring the intensity of a Hahn Spin-echo and its reduction as function of the gradient strength. This technique was established by Stejskal and Tanner.⁷ In our experiments, the sample cell used is of the Yamada-type⁸ and was modified by the authors.^{1,9} The preparation of the cells, the filling procedures and the complete high pressure set-up have been published in detail.^{9,10}

A Bruker MSL 300 NMR spectrometer operated at a proton frequency of 300 MHz in combination with a home built probe head was used for the measurements. The self-diffusion coefficients were calculated from the Fourier transformed second half of the spin echoes, the expression of which is given by

$$A(2\tau) = A(0)\exp(-2\tau/T_2)\exp(-(\gamma\delta g)^2 D(\Delta-\delta/3)) \quad (1)$$

where A is the amplitude of the echo, τ is the waiting period between the 90°- and 180°-pulse, T_2 is the spin-spin relaxation time of the proton under study, and γ is its gyromagnetic ratio, δ is the length of the field gradient pulse, its strength is given by $g = K \cdot I$ with K being the coil constant and I the pulse current, D is the self-diffusion coefficient to be measured, and Δ is the time between the leading edge of two gradient pulses. Generally, it is most reliable to determine D from a series of 10 to 12 spin echoes at increasing current I while keeping all other parameters in eq. (1) constant. The gradient coil was calibrated with water and *n*-pentanol at 293 K, the comparison of experimental error for self-diffusion data obtained from NMR method with that from the other techniques has been published previously.¹¹ The temperature was controlled by a metal sheathed ther-

mocouple at the position of the sample to ± 1 K. The pressures were determined with Bourdon gauges (Heise/Connecticut) to ± 1 MPa, or by strain gauges (Burster, Gernbach, Germany) to ± 0.2 MPa. The self-diffusion coefficients are judged reliable to $\pm 5\%$, and the reproducibility was better than $\pm 2\%$.

Results and discussion

The self-diffusion coefficients of α -humulene and myrcene measured are collected in Tables 1—2.

Table 1 Self-diffusion coefficients of α -humulene ($10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$)

T/K	p/MPa						
	0.1	5	10	30	50	75	100
372	7.95	7.34	6.85	5.56	4.36	3.31	2.53
324	3.38	3.04	2.82	2.22	1.64	1.18	0.837
297	1.58	1.46	1.30	0.956	0.699	0.415	0.256
274	0.681	0.625	0.558	0.364	0.222	0.158	

Table 2 Self-diffusion coefficients of myrcene ($10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$)

T/K	p/MPa						
	0.1	5	10	30	50	75	100
349	2.16	2.04	1.96	1.67			
323	1.56	1.50	1.46	1.23	1.05	0.870	0.735
297	1.12	1.08	1.04	0.888	0.730	0.593	0.495
274	0.748	0.715	0.685	0.594	0.496	0.408	0.341

The isobaric Arrhenius plots of the self-diffusion data for these two fluids are given in Fig. 1. As seen from this figure, the self-diffusion of α -humulene has a higher temperature dependence than that for myrcene. Fig. 2 shows the isotherms of myrcene. α -Humulene has a similar p -dependence and is not shown here.

From the temperature dependence of the dynamic properties of liquids in isobaric Arrhenius plots $(\ln D)_p \sim 1/T$, the activation energies ΔE_D^\ddagger are calculated by

$$\Delta E_D^\ddagger = -R \left(\frac{\partial \ln D}{\partial T^{-1}} \right)_p \quad (2)$$

where R is the gas constant, T is the absolute temperature, p is the pressure. The values of ΔE_D^\ddagger are often used for the intercomparison of the T -dependence of different liquids, although the underlying concept of the ac-

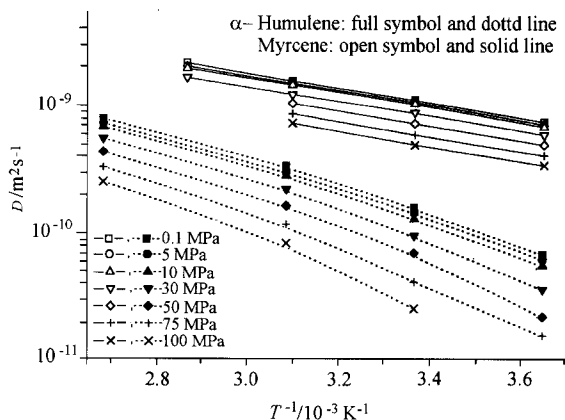


Fig. 1 Isobaric Arrhenius plots of the self-diffusion coefficient in neat fluids.

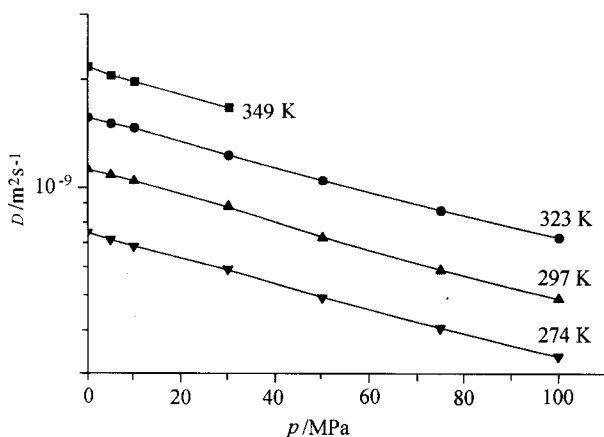


Fig. 2 Isotherms of the self-diffusion coefficient in neat myrcene.

tivation model was neither observed in any experimental studies nor in molecular dynamics simulation. In the activation model, one can obtain the activation volume ΔV_D^\ddagger from the slope of the isotherms. ΔV_D^\ddagger was defined by

$$\Delta V_D^\ddagger = -RT \left(\frac{\partial \ln D}{\partial p} \right)_T \quad (3)$$

As a comparison, the activation parameters ΔE_D^\ddagger (100 MPa, around 300 K) and ΔV_D^\ddagger for some fluids of low molecular weight are compiled in Table 3. The values of ΔE_D^\ddagger depend usually on the pressure and density, but ΔE_D^\ddagger is also determined by the molecular size and structure of diffusing substances. As seen from Table 3, the values of ΔE_D^\ddagger and ΔV_D^\ddagger for myrcene are very similar to the data found for benzene and tetramethylsilane, while ΔE_D^\ddagger (100 MPa) and ΔV_D^\ddagger (297 K) for α -humulene are $27.6 \text{ kJ} \cdot \text{mol}^{-1}$ and $49.6 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$, respectively. These values are much greater than those for other fluids because of: (1) α -Humulene has larger molecular size and weight; (2) The α -humulene molecule may be more deformable, since it has a large ringed structure. However, Table 3 indicated that the typical hydrogen bonded liquids like water and methanol show smaller activation volumes and these two liquids have significantly higher activation energies at constant pressure.

Table 3 Activation parameters for some fluids

Substance	$\Delta E_D^\ddagger / \text{kJ} \cdot \text{mol}^{-1}$	$\Delta V_D^\ddagger / 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$	Ref.
	(100 MPa)	(50—100 MPa)	
α -humulene	27.6 (297—372 K)	49.6 (297 K)	this work
myrcene	11.6 (274—323 K)	19.2 (297 K)	this work
water	17.4 (300 K)	1 (275 K)	12
methanol	12.7 (300 K)	4 (292 K)	3
methane	5.6 (300 K)	12 (273 K)	13
carbon dioxide	7.7 (300 K)	12.5 (298 K)	2
tetramethylsilane	10.1 (298—348 K)	17.4 (298 K)	14
benzene	13.9 (298—313 K)	14.5 (298 K)	15

A further data analysis by other models is not possible at the moment because of the lack of supplementary thermodynamic and dynamic data at elevated pressures.

Only a few intradiffusion coefficients for α -humu-

lene and myrcene in CO_2 could be measured. The solubility of these substances in CO_2 is fairly small¹⁶ and their complex proton spectra yield very weak signals only. The intradiffusion coefficients D_{ii} obtained are as fol-

lows:

(1) $D_{ii} = 4.0 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ (298 K, 75 MPa), $5.4 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ (333 K, 75 MPa) for diffusion of α -humulene in CO_2 . The concentration of α -humulene in the mixture is 3%.

(2) $D_{ii} = 6.5 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ (298 K, 50 MPa) for diffusion of myrcene in CO_2 . The concentration of myrcene in the mixture is 5%.

It should be noted that the above mentioned concentrations were prepared by weighing, while the real solubilities of these compounds in CO_2 are certainly less than these values, and we have not found the exact data from literature. Therefore, in this case the overall error of D_{ii} is estimated about \pm (20%—30%).

Comparison with the data in Tables 1—2 shows that the values of D_{ii} are about one order of magnitude higher than those for the pure components at the same T , p -ranges. These results are useful references for the design of supercritical extraction plants.

Conclusions

The self-diffusion of neat fluids α -humulene and myrcene were studied. The measured data obtained were analyzed by the activation model and compared with those for other fluids. The intradiffusion coefficients D_{ii} of these two substances in carbon dioxide were also determined. The results indicate that the values of D_{ii} are about one order of magnitude higher than those for pure components at the same T , p -ranges. This behavior would be typical for other similar complex molecules diffusing in CO_2 .

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