THE SOLUBILITY OF CO_2 AND N_2O IN SOME C_6 HYDROCARBONS AT HIGH PRESSURES

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abstract: In this study we have studied the solubility of CO_2 and N_2O in a series of C_6 hydrocarbons, namely: n-hexane, cyclohexane and metyl-cyclopentane by pressure up to 35 bar and temperatures in a range of $0 \div 25^0C$. In all investigated systems we have found remarkable values of gas solubility with specific features that evidence some effects depending of the structure of solvents. The regular solutions theory was employed as theoretical model for calculation the solubility of gases in the investigated solvents.

Introduction

This work is a continuation of a programme initiated for some years ago concerning the solubility of gases in a wide category of organic solvents: hydrocarbons, alchols, ketones at high pressure and a wide domain of temperatures [1÷3].

Materials and Methods

The experimental device and the detailed description of working method is presented in a separate research [4]. By using of this experimental method we have performed a study concerning the influence of the isomeric effects on gas solubility. In this purpose we have selected two cyclic hydrocarbons namely cyclohexane and metyl-cyclopentane and two gases with likewise properties, CO_2 and N_2O. As a reference we have select the solubility of these gases in n-hexane. The working domain was temperatures among 273.16÷298.16 K and pressures up to 50 bar. The finding of experimental data for the mentioned system is very difficult because in this temperature interval the vapour pressures of all solvents possess considerable values. Moreover, because the solubility are obtained by measurement the amount of disrobed gas after vacuum détente of gas saturated liquid was necessary to cool the gathering ampoule at $-20\ ^0C$ to condense the vapours of the solvent.

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Results and Discussion

The experimental values of gas solubility are presented in Table 1 for the systems solvents with CO_2 and in Table 2 for the systems solvents with N_2O.

Table 1. Experimental values of gas solubility.

n-hexane + CO_2			Metyl-cyclopentane + CO_2			Cyclohexane + CO_2		
T (K)	P (bar)	x_{CO2}	T (K)	P (bar)	x_{CO2}	T (K)	P (bar)	x_{CO2}
	37.43	0.450						
	36.26	0.380					29.79	0.525
	32.04	0.365		28.32	0.618		21.65	0.337
	30.38	0.331		21.26	0.439		15.28	0.250
273.16	21.85	0.219	273.16	11.27	0.240	273.16	9.80	0.205
	20.58	0.204		6.56	0.206		5.39	0.151
	12.74	0.122						
	5.68	0.058						
	44.00	0.508		32.00	0.597		29.40	0.448
	39.00	0.421		22.44	0.389		22.93	0.344
278.16	29.10	0.281	278.16	15.19	0.288	278.16	16.75	0.256
	21.46	0.194		10.09	0.212		11.56	0.215
	8.13	0.071		5.88	0.172		6.86	0.165
				5.68	0.163			
	41.45	0.379		31.75	0.538		33.41	0.499
	41.25	0.368		21.65	0.362		26.26	0.346
283.16	30.96	0.260	283.16	18.71	0.290	283.16	19.60	0.264
	21.75	0.176		12.83	0.243		12.25	0.209
	12.54	0.094					8.13	0.179
	44.78	0.351		29.69	0.487		41.16	0.548
	41.25	0.340		22.54	0.398		31.55	0.393
288.16	33.51	0.254	288.16	13.52	0.273	288.16	22.65	0.313
	30.87	0.222		9.99	0.246		13.23	0.211
	21.75	0.152		5.48	0.166		7.44	0.159
	9.99	0.073						
	52.33	0.350						
	41.65	0.265						
	41.35	0.261		35.08	0.422		42.82	0.400
	31.85	0.203		26.06	0.315		32.73	0.321
298.16	31.65	0.201	298.16	17.83	0.231	298.16	22.34	0.222
	26.75	0.169		11.95	0.175		12.74	0.147
	15.68	0.100		5.88	0.126		7.54	0.114
	11.85	0.081						
	7.05	0.046						

One can remark considerable values of gas solubility for all investigated systems. Concerning the absolute values of solubility's expressed as molar fractions one observe noteworthy features that spotlight the influence of structural effects on gas solubility.

The smaller values of solubility were observed for systems n-hexane + CO_2 and n-hexane + N_2O. For all investigated temperatures and pressures the solubility of CO_2 in n-hexane is considerable greater as for N_2O in the same solvent.

For the other systems (cyclohexane and metyl-cyclopentane + CO_2 and N_2O respectively) the solubility are much greater. For example, for the system metyl-cyclopentane + CO_2 at temperature of 273.16 K the molar fraction of CO_2 has a value of about 0.6 and in similar condition the solubility of CO_2 in cyclohexane exceed the value 0.5.

For the systems cyclohexane and metyl-cyclopentane + N_2O the solubilities reach to values of 0.8. This means the appearance of a new equilibrium: the solvent dissolved in the compressed gas, these increased values on the result of the interaction between the molecules of gas and those of the hydrocarbons.

For all investigated systems one observe at higher pressures and lower temperatures considerable deviation from Henry law. At 298.16 K the dependence $P = f(x_2^l)$ is a straight line and therefore the Henry law is respected. A proof of this assertion is the fact that the values of solubility obtained by extrapolation at $P = 1$ atm are $(x_2^l)_{CO2}=0.41$ and $(x_2^l)_{N2O}=0.40$.

A rigorous method for the prediction of gas solubility requires a valid theory of solution but such of theory is not available. For a semiempirical description of non-polar systems the theory of regular solution can serve as a basis for the correlation of gas solubility [5÷7].

Table 2. Experimental values of gas solubility.

n-hexane + N_2O			Metyl-cyclopentane + N_2O			Cyclohexane + N_2O		
T (K)	P (bar)	x_{N2O}	T (K)	P (bar)	x_{N2O}	T (K)	P (bar)	x_{N2O}
273.16	29.6	0.486	273.16	27.73	0.810	273.16	25.67	0.619
	24.79	0.351		24.79	0.771		20.67	0.510
	19.70	0.275		19.6	0.639		15.48	0.392
	15.20	0.212		14.5	0.520		10.68	0.274
	9.70	0.145		9.8	0.410		6.17	0.170
	6.08	0.084		4.6	0.248			
278.16	30.9	0.393	278.16	26.65	0.720			
	24.6	0.309		21.26	0.586			
	19.11	0.235		14.40	0.435			
	14.8	0.184		10.29	0.363			
	10.09	0.131		5.29	0.221			
	5.78	0.092						
283.16	30.38	0.351	283.16	26.26	0.621	283.16	25.97	0.493
	24.89	0.292		20.6	0.498		20.67	0.409
	20.09	0.229		15.68	0.423		15.77	0.321
	14.99	0.167		10.19	0.291		10.97	0.210
	10.19	0.116		5.97	0.203		6.07	0.140
	5.68	0.085						
288.16	31.75	0.311	288.16	31.06	0.610	288.16	26.36	0.448
	26.56	0.259		24.89	0.538		20.97	0.362
	21.85	0.221		19.79	0.428		15.87	0.291
	16.46	0.176		14.7	0.316		10.38	0.194
	10.39	0.117		9.89	0.240		5.97	0.133
				5.39	0.145			
298.16	34.50	0.287	298.16	27.63	0.451	298.16	27.83	0.404
	29.98	0.258		21.75	0.378		21.36	0.310
	25.48	0.219		16.17	0.290		15.97	0.247
	19.89	0.168		11.56	0.228		10.29	0.177
	14.50	0.133		6.46	0.162		6.0	0.122
	8.03	0.072						

For that purpose to consider a gas dissolved isothermally in a liquid far from its critical temperature. The dissolution process is accompanied by a change in enthalpy and in entropy as in the case when two liquids are mixed. The dissolution of a gas in a liquid is accompanied by a large reduction in volume, since the volume of the solute in the condensed phase is much smaller then that in the gas phase. This large decrease in volume differentiates the dissolution of a gas from the dissolution of a liquid. In order to apply

regular solution theory which assess no volume change – it is necessary to condense firstly the gas up to a volume close to the partial molar volume of a solute dissolved in a certain solvent. The isothermal dissolution process is then considered in two steps:

$$\Delta G = \Delta G_1 + \Delta G_2 \tag{1}$$

$$\Delta G_1 = RT \ln {f_2^l}/{f_2^0} \tag{2}$$

$$\Delta G_2 = RT \ln \gamma_2^l \cdot x_2^l \tag{3}$$

In the first step the gas is isothermally condensed up to a hypothetical state having a volume as a liquid. In the second step this hypothetical liquid is dissolved in the solvent. Since the solute from the liquid solution is in equilibrium with the gas at unit fugacity, the equation of equilibrium is:

$$\Delta G = 0 \tag{4}$$

The regular solution theory allows the calculation of the activity coefficient of the gaseous solute with the relation:

$$RT \ln \gamma_2^l = V_2^l \left(\delta_1 - \delta_2 \right)^2 \cdot \phi_1^2 \tag{5}$$

The substitution of equations (1), (2) and (5) into equation (4) gives the solubility at 1 atm partial pressure:

$$\frac{1}{x_2^l} = \frac{f_2^l}{f_2^0} \exp \frac{V_2^l \cdot \left(\delta_1 - \delta_2 \right)^2 \cdot \phi_1^2}{RT} \tag{6}$$

This correlating scheme involves three parameters for the gaseous component as a hypothetical liquid: the fugacity, the volume and the solubility parameter. These parameters are all temperature dependent; however the theory the theory of regular solution assumes that at constant composition $\ln \gamma_2^l$ is proportional with $1/T$ and therefore the quantity $V_2^l \cdot \left(\delta_1 - \delta_2 \right)^2 \cdot \phi_1^2$ is not temperature dependent. Thus, any convenient temperature may be used to specify V_2^l and δ_2 provided the same temperature is used for δ_1 and V_1^l. The most convenient temperature is 25 ^{0}C. The fugacity of the hypothetical liquid must be however treated as a function of temperature. The small effect of solvent on V_2^l need not be considered for the purposes of this work because the volume change is much smaller than that corresponding to step 1.

The fugacity of the hypothetical liquid solute at a pressure of 1 atm depends only on the temperature and properties of the solute and is independent of the properties of the solvent. It is possible therefore to apply the theorem of corresponding states and to show that the reduced fugacity of the hypothetical liquid solute is a universal function of the reduced temperature. For the reduced temperature range 0.7 to 0.8 vapor-pressure data for liquefied gases (such as CO_2 and N_2O) were used to obtain a plot of ${f_2^l}/{P_c}$ versus T/T_c (Fig. 1) [8].
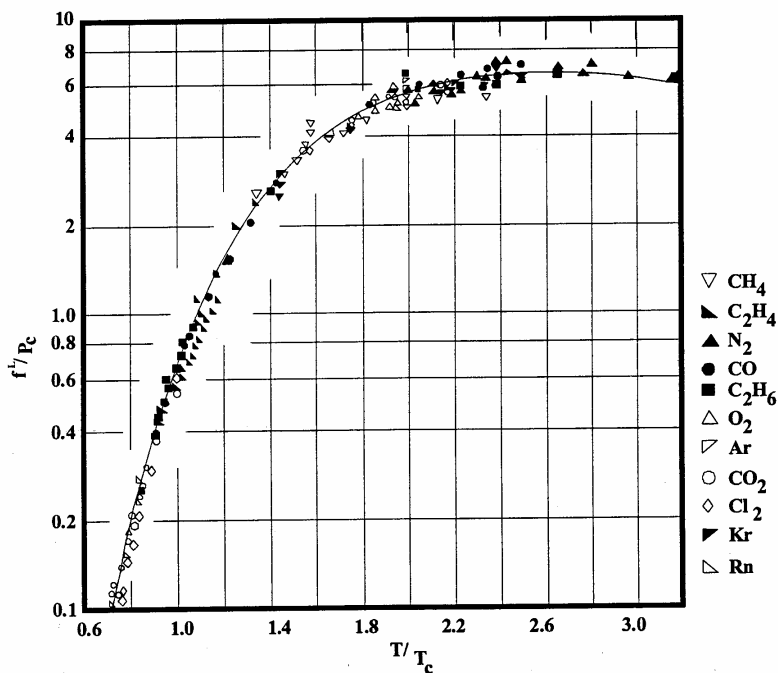
Fig. 1: *Fugacity of a hypothetical liquid at partial pressure of 1 atm.*

For the calculation that we performed at partial pressure of 1 atm $\left(f_2^l = 1 \right)$, the molar fraction of the solute in the liquid phase is much smaller as unity and in this case we consider the volume fraction $\phi_1 = 1$.

The results obtained by application the regular solution model are presented in the Table 3.

Table 3. The calculated solubility of gases by application of the regular solution model.

Gas	Solvent	δ_1 $(cal/cm^3)^{1/2}$	δ_2 $(cal/cm^3)^{1/2}$	V_2^l (cm^3/mol)	T_c (K)	P_c (bar)	f_2^l (bar)	x_2^l
CO_2	n-hexane	7.30	6.0	55	304.25	73	29.2	0.0292
CO_2	cyclohexane	8.20	6.0	55	304.25	73	29.2	0.0220
CO_2	metyl-cyclopentane	8.0	6.0	55	304.25	73	29.2	0.0240
N_2O	n-hexane	7.30	7.6	36	309.65	71.7	43.02	0.0230
N_2O	cyclohexane	8.20	7.6	36	309.65	71.7	43.02	0.0232
N_2O	metyl-cyclopentane	8.0	7.6	36	309.65	71.7	43.02	0.0227

The calculated values are in good concordance with those obtained by application the Henry law in the form $x_2^l = 1 \big/ f_2^g$.

Conclusions

By using of a genuine experimental device one have determined the solubility of CO_2 and N_2O in three non-polar solvents: n-hexane, cyclohexane and metyl-cyclopentane at pressure up to 50 bar and in the temperature domain of 273.16 ÷298.16 K. We have found remarkable values for solubility of gases in all organic solvents with great deviation from Henry law, especially for low temperatures. For correlation of gas solubility we have applied the regular solution model.

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