

SOLUBILITY OF HYDROCARBONS IN A WATER - MINERAL ACID SYSTEM. MODEL OF CALCULATION

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Introduction

Hydrocarbons (RH) solutions in mineral acids is widely used in various technological processes. The technology of processing of liquid products coking coal, which consist of aromatic RH, olefines and alkanes includes a stage of treatment by concentrated sulphuric acid. Therefore it is important from technological and ecological points of view to know the solubility of RH and their derivative in a water - mineral acid systems in the whole range of it compositions. However up to recent time such data are practically absent, especially for range of high concentration of acids. Determination of RH solubility have difficulties which connect with its small solubility, large viscosity of systems and large reactivity of RH in concentrated mineral acids, especially olefines and benzene derivatives. The possibilities of calculation of solubility connected only to the equation of Sechenov $\lg(S_0/S) = K c$, which describes only diluted electrolyte solutions.

Solubility of RH of a various structure in a water-sulphuric acid, water-nitric acid and water-phosphoric acid systems over the whole range compositions of these systems from 0 to 100% was studied by us and the model of calculation of solubility RH in a water-mineral acid systems was developed.

Experimental

The hydrocarbons solubilities was obtained at 298 K as limiting distribution coefficients between the gas and solution, $\alpha = C_{gas}/C_{sol}$ at $C_{gas} \rightarrow 0$. Value α^{-1} is equal to solubility at given RH concentration in the gas phase and coincides with the Ostwald coefficient, which is widely used measure of volatile substrates solubility. Measurements were performed by gas-liquid chromatography method. The concentration of RH in equal volumes of gas and liquid phases was analysed at condition of equilibrium distribution of substrate between

two phases. In each case it was made 5-7 measurements. The reproducibility of results was within $\pm 7-10\%$.

Results and Discussion

Experimental data have been obtained [1-3] for helium, methane, propane, n-hexane, isobutane, isopentane, cyclopentane, cyclohexane, methylcyclopentane and benzene in a water-sulphuric acid system; methane, ethane, propane and n-hexane in water-nitric acid system; methane, propane, cyclopentane and cyclohexane in water-phosphoric acid system over the whole range of mixture composition from 0 to 100% of acid at 298 K. On the basis of these and literature data on solubility of hydrogen, oxygen, nitrogen, benzene and other nonelectrolyte (NE) following equations have been established.

1. For all investigated NE the linear dependence is fulfilled:

$$\lg(\alpha_a/\alpha_w) = a + b V_2^0, \quad (1)$$

where α_w и α_a - distribution coefficients of NE for water and acid correspondingly, V_2^0 - partial molar volume of NE in water [4]. Coefficients of equation (1) are:

	H ₂ SO ₄	HNO ₃	H ₃ PO ₄
a, mole/cm ³	0.56	0.37	1.2
b 10 ²	2.2	-2.9	-0.82

2. Excess value $(\lg\alpha)^E$, which is determined as $(\lg\alpha)^E = \lg\alpha - x_a \lg\alpha_a - x_w \lg\alpha_w$ linearly depends against relative compression of a solution ($V^E/V = V - x_a V_a - x_w V_w$). The equation:

$$(\lg\alpha)^E = L V^E/V \quad (2)$$

fulfills for all studied systems quantitatively despite significant differences of acids influence on RH solubility [1-3]. As example the data on propane it is demonstrated on Fig.1. Propane solubility increase (α decrease, salting-in) in nitric acid over the whole range of system

composition, decrease (α increase, salting-out) in phosphoric acid and the extremum takes place in sulphuric acid (salting-out at small and salting-in at large of acid concentration). Good correspondence between calculated (lines) and experimental (points) value α can be seen on Fig. 1.

3. The values of L parameter are directly proportional V_2^0 :

$$L = c + d V_2^0 \quad (3)$$

Coefficients of equation (3) are:

	H ₂ SO ₄	HNO ₃	H ₃ PO ₄
c, mole/cm ³	-4.8	-5.8	-8.8
d 10 ²	-3.9	6.0	-10

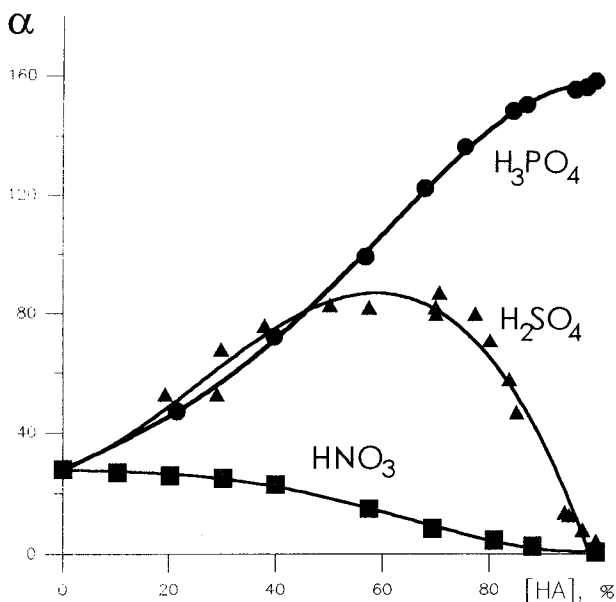


Figure 1. The influence of acid concentration on propane solubility at 298 K in the systems H₂O-HNO₃ (■), H₂O-H₂SO₄ (▲) and H₂O-H₃PO₄ (●). The lines correspond according to equation (2).

Conclusions

The data obtained and relationships established (eq. 1,2,3) open possibility of a quantitative prediction of RH solubility over the whole range of water - mineral acid systems compositions, as shown on Fig.2 for benzene and isobutylene in H₂O-H₂SO₄. The solubility of these

substrates at high acid concentrations is not possible to measure because of their high reactivity in this system.

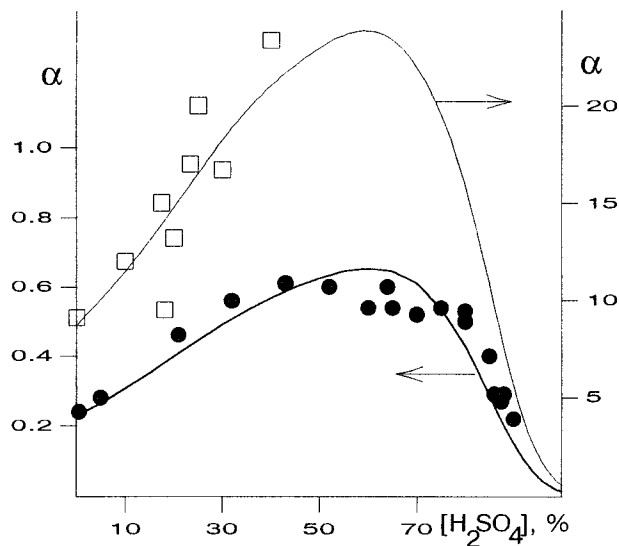


Figure 2. Application of the model developed to the calculation of the benzene (●) and isobutene (□) solubility at 298 K in the system H₂O-H₂SO₄. The lines correspond according to equations (1-3), the points - experimental data [5-9].

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