Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1994, **4**(1), 27–28
Mendeleev Communications

Propane Solubility in Aqueous Mineral Acids (0–100%): a Significant Difference in the Solvating Properties of H_2SO_4, HNO_3 and H_3PO_4

Elisei S. Rudakov, Alexander I. Lutsyk and Gennadii G. Gundilovich

L. M. Litvinenko Institute of Physical-Organic and Coal Chemistry, Academy of Sciences of Ukraine, 340114 Donetsk, Ukraine. Fax: +7 0622 553 542

Unexpectedly high differences in propane solubility in the systems HNO_3–H_2O (salting-in), H_3PO_4–H_2O (salting-out) and H_2SO_4–H_2O (salting-out at low H_2SO_4 concentrations and salting-in at high concentrations) have been revealed, and the data quantitatively interpreted within the framework of the previously suggested equation relating the excess amounts of solubility with the molar volume of a system; the general nature of these equations for systems of this type has been demonstrated.

Solutions of hydrocarbons (RH) in concentrated mineral acids (HA) are widely used in various chemical processes. However, until recently, experimental data on the solubility of RH in the systems water–acid in the range 0–100% of HA were almost lacking; the possibilities of calculating the solubility were associated[1,2] only with the Sechenov equation (1),

$$\lg (S_0/S) = K \cdot c \qquad (1)$$

which is, strictly speaking, applicable to dilute solutions only. Here S_0 and S are the solubilities of non-electrolytes (NE) in water and in an electrolyte solution with concentration c and K is the salting-out coefficient.

Recently[3] we suggested equation (2) for the solubility of NE in the system H_2SO_4–H_2O:

$$(\lg \alpha)^E \equiv \lg \alpha - x_w \lg \alpha_w - x_a \lg \alpha_a = K^* \cdot c_{ion} = LV^E/V \qquad (2)$$

where α is the limiting distribution coefficient of NE between the gas and the solution, $\alpha = [NE]_g/[NE]_s$ at $[NE]_g \to 0$ (the value α^{-1} equals the solubility of NE at its given concentration in the gas phase and coincides with the Ostwald coefficient). This equation relates the excess value of $(\lg \alpha)^E$ [determined taking into account the solubility of NE in pure individual components (in water and in 100% H_2SO_4)] with the concentration of ions c_{ion} or with the excess molar volume of the solvent $V^E = V - x_w V_w - x_a V_a$, where x_w and x_a are the molar fractions of water and acid in the mixture; α_w, α_a and α are the distribution coefficients of substrate for water, 100% acid and the solution; V^E/V is the relative solution compression due to interactions between the components; and K^* and L are coefficients which are constant for the given acid and electrolyte. One can see that this equation incorporates the Sechenov equation as a specific case (at $x_a \to 0$) and allows one to analyse the solubility based on the available data for the solvent densities.

In order to verify the applicability of this equation to other systems, this work studies the solubility of propane in the systems HNO_3–H_2O, H_3PO_4–H_2O and H_2SO_4–H_2O, allowing measurements to be performed over the whole range of compositions between 0 and 100% of acid. The experimental data were obtained by means of the static GLC method[4] as the distribution coefficients α. The reproducibility of α values was within $\pm 7\%$. Since at 298 K liquid 100% H_3PO_4 is in the metastable state, a special investigation of the stability of this state and of the reproducibility of the results was undertaken. It was revealed that the α values coincided for H_3PO_4 solutions prepared in different ways and did not depend on the exposure time (from 2–3 to 80 h); there were no inflexions in the $\lg \alpha$ *vs.* $1/T$ plot for methane at 291–338 K on changing from metastable to stable systems (ΔH of dissolution = 8.5 kJ mol^{-1}).

H_2SO_4, HNO_3 and H_3PO_4 are «strong» inorganic oxygen-containing acids. However, the influence of acid concentration on α for propane in the systems of interest has proved to be remarkably different (Fig. 1): the α growth (solubility decrease, salting-out) over the whole range of compositions for the system H_3PO_4–H_2O; the α decrease (solubility increase, salting-in) for nitric acid; and the presence of an extremum in the dependence α – acid concentration for the system H_2SO_4–H_2O. The Sechenov equation is not fulfilled for any of the systems. All the data obtained are described quantitatively by equation (2) (Figs. 1 and 2) suggesting the general applicability of this equation for the systems water–mineral acid. The significant

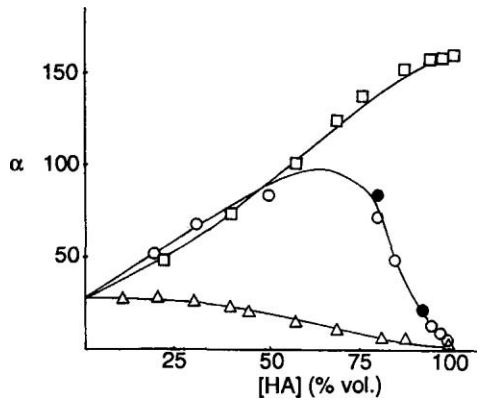

Fig. 1 The influence of acid concentration on propane solubility at 298 K in the systems H_2O–HNO_3 (Δ), H_2O–H_2SO_4 (○) and H_2O–H_3PO_4 (□). The lines correspond to calculations according to equation (2). ● – our data (ref. 5).

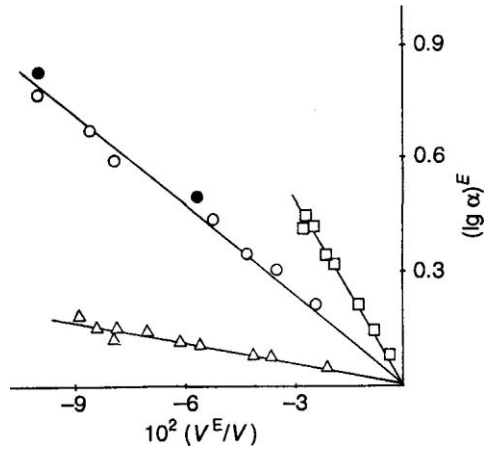

Fig. 2 Treatment of experimental data for propane solutions in the systems H_2O–HNO_3 (Δ), H_2O–H_2SO_4 (○) and H_2O–H_3PO_4 (□) according to equation (2). The values of V^E/V have been calculated from the densities of solutions of the acids.[6,7]

differences in the concentration effects of nitric, phosphoric and sulfuric acid on propane solubility are due to the changes in α_a and L.

The second marked difference in the systems under study consists of the fact that the α_a value for propane in phosphoric acid is almost two orders of magnitude lower than for H_2SO_4 and HNO_3 as evident from the following data.

Solvent	H_2O	HNO_3	H_2SO_4	H_3PO_4
α_a	26	0.66	3.4	158
L	—	−1.7	−8.0	−16

It is reasonable to assume that the decrease in propane solubility in the sequence $HNO_3 > H_2SO_4 > H_3PO_4 > H_2O$ is due to an increase in the solvent internal pressure determining the energy for the formation of a cavity of molecular size. The latter is characterized by the Hilderbrant solubility parameter,[8] $\delta = (E/V)^{1/2}$, where E is the internal heat of evaporation and V is the molar volume of the liquid. We used this approach, which is usually applied to non-associated media,[8,9] in order to process our and literature data on the solubility of propane in various individual solvents.[2] The results thus obtained (Fig. 3) evidence the validity of our assumption. The high solubility (low value of α) of hydrocarbons in 100% nitric acid is in accordance with the

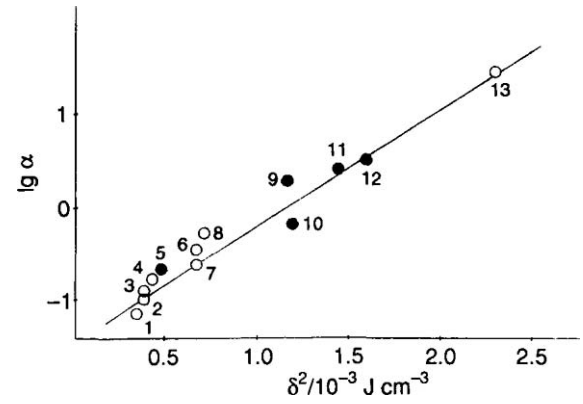

Fig. 3 The dependence of lg α on the Hildebrant parameter (δ) for solutions of propane in benzene (1), acetone (2), dioxane (3), acetic acid (4), trifluoroacetic acid (5), acetic anhydride (6), ethanol (7), dimethyl sulfoxide (8), ethylene glycol (9), nitric acid (10), formamide (11), sulfuric acid (12) and water (13). Blackened points correspond to data obtained in this study, others were calculated according to ref. 2. The δ values were calculated according to ref. 10.

fact that the δ value for nitric acid is similar to those for organic solvents. The anomalously low propane solubility in 100% H_3PO_4 suggests an extraordinarily high intermolecular interaction energy in this liquid. The low pressure of H_2O vapours over the system P_2O_5–H_3PO_4 used for drying of reagents is an indirect confirmation of this fact. There are no data on the evaporation heat or boiling point of H_3PO_4. An estimate based on the line in Fig. 3 gives the values $\delta \cong 54$ J$^{1/2}$ cm$^{-3/2}$(40), $E \cong 154$ kJ mol^{-1} (86), and b.p. $\cong 1.3 \times 10^3$ K (603). For comparison, similar values for H_2SO_4 are given in parentheses.

Interestingly, there is a nearly linear dependence between the L values, found from the slopes of the lines in Fig. 2, and lg α_a: $L = -0.25 - 0.10 \lg \alpha_a$. Hence, equation (2) can be represented as equation (3),

$$(\lg \alpha)^E \equiv x_w \lg \alpha_w + x_a \lg \alpha_a + (C_1 + C_2 \cdot \lg \alpha_a) V^E/V \quad (3)$$

where C_1 and C_2 are constants for a given hydrocarbon.

The results of this work indicate that equation (2), suggested for solutions of non-electrolytes in sulfuric acid, is of general character. Despite the significant differences in the experimentally observed influence of the solvent, this equation is an efficient tool for analysing the data on the solubility of non-polar compounds in the systems mineral acid–water.

References

1 E. I. Konnik, *Usp. Khim.*, 1977, **46**, 1097 (*Russ. Chem. Rev.*, 1977, **46**, 577).
2 R. Battino, *Solubility Data Series*, 1986, **24**.
3 E. S. Rudakov, A. I. Lutsyk and S. Yu. Suikov, *Zh. Fiz. Khim.*, 1987, **61**, 1153 (*Russ. J. Phys. Chem.*, 1987, **61**, 601).
4 E. S. Rudakov and A. I. Lutsyk, in *Mezhmolekulyarnye vzaimodeistviya i reaktsionnaya sposobnost' organicheskikh soedinenii (Intermolecular interactions and reactivity of organic compounds)*, ed. E. V. Titov, Naukova Dumka, Kiev, 1983, 3 (in Russian).
5 E. S. Rudakov and A. I. Lutsyk, *Zh. Fiz. Khim.*, 1979, **53**, 1298 (*Russ. J. Phys. Chem.*, 1979, **53**, 731).
6 *International Critical Tables*, McGraw-Hill Book Co., New-York, 1928.
7 E. P. Egan Jr. and B. B. Luff, *Ind. Eng. Chem.*, 1955, **47**, 1277.
8 J. H. Hildebrant and R. L. Scott, *Regular Solutions*, Prentice-Hall, New-York, 1962.
9 E. S. Rudakov, *Termodinamika mezhmolekulyarnogo vzaimodeistviya (Thermodynamics of intermolecular interaction)*, Nauka, Novosibirsk, 1968 (in Russian).
10 R. C. Reid, J. M. Prausnitz and T. K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill Book Co., New-York, 1977.

Received: Moscow, 18th June 1993
Cambridge, 20th September 1993; Com. 3/03597B