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Solubility and Thermodynamic functions of imidazole in pure solvents and their binary mixtures at (293.15 to 313.15) K

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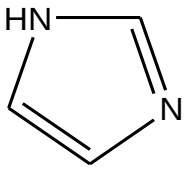
ABSTRACT

Solubility of imidazole in water, methanol and in water-methanol binary mixtures have been experimentally measured using a gravimetric method at temperatures (293.15, 295.15, 298.15, 300.15, 303.15, 305.15, 308.15, 310.15 & 313.15) K. Solubility values were correlated by the Apelblat equation. The combined NIBS (nearly ideal binary solvent)-Redlic-Kister equation is used to fit experimental solubility data at constant temperature. Thermodynamic functions including ΔH^0_{sol}, ΔG^0_{sol}, and ΔS^0_{sol} of solution of imidazole are obtained from the modified van't Hoff equation.

Keywords: Imidazole, Solubility, Apelblat equation, NIBS, Solution thermodynamics.

I. INTRODUCTION

The molecular structure of a imidazole under study is



Imidazole

Heterocyclic compounds play an important role in various areas, of these imidazole is one of the versatile compound used in pharmaceuticals. It is planner 5-memebered ring containing two nitrogen atoms. Molecular formula is C3H4N2 and is amphoteric in nature. It is used for preparing various types of drugs. Imidazole is a building unit of many drugs. Imidazole and its derivatives acts as antifungal, anti-microbial, analgesic, anti-inflammatory, anti-tubercular, anticancer, anticoagulants, anti-bacterial, anti-viral, antidiabetic, anti-malerial activity etc [1]. Imidazole is highly polar molecule having dipole moment [2] 3.61 D. Solubility is an essential physicochemical aspect in drug discovery and development [3].

Urszula Domanska and Marta Kozlowska determined the solubility of imidazole in pure ethanol, propan-1-ol, Propan-2-ol, butan-1-ol, butan-2-ol, 2-methyl propan-2-ol, hexan-1-ol and dodecan- 1-ol [4]. And also in ethers like dipropyl ether, dibutyl ether, dipentyl ether, methyl 1,1- dimethylethyl ether, methyl 1,1-dimethypropyl ether [5]. However there is no data available on solubility of imidazole in pure methanol and water-methanol for the complete binary composition range.

In this work the systematic study of solubility of imidazole in water + Methanol binary solvents over the entire composition range from 0 to 1 mole fraction, at temperatures (293.15 to 313.15) K. The solubility values were correlated by the apelblat equation. The thermodynamic functions for imidazole solution were calculated using modified van't Hoff equation.

II. EXPERIMENTAL SECTION

Material

In all experiments, triple distilled water was used. Imidazole was supplied by spectrochem with purity (Imidazole) 99.5 %. Methanol supplied by Fisher Scientific with purity 99.5 %.

Apparatus and Procedure

The solubility of imidazole was measured using an apparatus similar to that described as in the literature [6-8]. An excess amount of imidazole was added to the binary solvent mixture prepared by weight (Scale-Tec) with an uncertainty of ± 0.1 mg, in a specially designed 100 mL double jacketed flask. Water was circulated at constant temperature between the outer and inner walls of the flask. The temperature of the circulating water was controlled by thermostat within (± 0.1) K. The solution was continuously stirred using a magnetic stirrer for long time so that equilibrium is assured, and the temperature of solution is same as that of circulating water; the stirrer was switched off; and the solution was allowed to stand for 1 hour. Then a fixed quantity of the supernatant liquid was withdrawn from the flask in a weighing bottle with the help of pipette which is hotter than the solution. The weight of this sample was taken and kept in an oven at 343 K until the whole solvent was evaporated and the residue was completely dry. This was confirmed by weighing two or three times until a constant weight was obtained after keeping the sample in an oven for another 30 min every time. The solubility has been calculated using weight of solute and weight of solution. Each experimental value of solubility is an average of at least three different measurements. The saturated mole fraction solubility(x_B), initial the mole fraction of methanol (x_C^0), were calculated using usual equations [6-8].

Table 1. Experimental $x_{B(exp.)}$ and calculated $x_{B(cal.)}$ values of mole fraction solubility for various initial mole fractions, x_C^0, of methanol at temperatures (293.15 to 313.15) K and Pressure 101.32 kPa[a].

T/K	x_C^0	$x_{B(exp.)}$	$x_{B(cal.)}$	RD	T/K	$x_{B(exp.)}$	$x_{B(cal.)}$	RD
293.15	0.0000	0.3556	0.3551	0.0015	305.15	0.4532	0.4531	0.0002
	0.0588	0.3560	0.3559	0.0003		0.4453	0.4455	-0.0004
	0.1232	0.3590	0.3594	-0.0013		0.4471	0.4452	0.0043
	0.1942	0.3683	0.3687	-0.0010		0.4526	0.4506	0.0044
	0.2726	0.3836	0.3407	0.1120		0.4611	0.4101	0.1106
	0.3599	0.4001	0.3995	0.0014		0.4756	0.4728	0.0060
	0.4575	0.4196	0.4186	0.0024		0.4910	0.4876	0.0070
	0.5675	0.4296	0.4297	-0.0002		0.5028	0.4993	0.0070
	0.6922	0.4386	0.4392	-0.0015		0.5123	0.5099	0.0047
	0.8350	0.4492	0.4502	-0.0024		0.5182	0.5172	0.0019
	1.0000	0.4622	0.4622	0.0000		0.5254	0.5244	0.0018
295.15	0.0000	0.3699	0.3710	-0.0030	308.15	0.4789	0.4782	0.0015
	0.0588	0.3713	0.3705	0.0023		0.4695	0.4686	0.0019
	0.1232	0.3772	0.3739	0.0085		0.4657	0.4657	0.0000
	0.1942	0.3856	0.3826	0.0078		0.4704	0.4702	0.0006
	0.2726	0.3941	0.3523	0.1060		0.4796	0.4270	0.1096
	0.3599	0.4132	0.4116	0.0039		0.4924	0.4913	0.0022

	0.4575	0.4295	0.4299	-0.0010		0.5014	0.5052	-0.0074
	0.5675	0.4417	0.4413	0.0009		0.5116	0.5166	-0.0098
	0.6922	0.4509	0.4511	-0.0006		0.5204	0.5271	-0.0129
	0.8350	0.4621	0.4608	0.0027		0.5317	0.5353	-0.0067
	1.0000	0.4707	0.4713	-0.0012		0.5399	0.5430	-0.0058
	0.0000	0.3948	0.3953	-0.0012		0.4919	0.4950	-0.0063
	0.0588	0.3871	0.3926	-0.0143		0.4773	0.4841	-0.0142
	0.1232	0.3871	0.3956	-0.0220		0.4723	0.4791	-0.0144
	0.1942	0.3947	0.4033	-0.0218		0.4775	0.4829	-0.0112
	0.2726	0.4076	0.3698	0.0929		0.4885	0.4382	0.1029
298.15	0.3599	0.4255	0.4298	-0.0101	310.15	0.5023	0.5036	-0.0027
	0.4575	0.4443	0.4471	-0.0062		0.5179	0.5169	0.0019
	0.5675	0.4575	0.4587	-0.0025		0.5295	0.5282	0.0025
	0.6922	0.4696	0.4689	0.0013		0.5392	0.5384	0.0014
	0.8350	0.4775	0.4771	0.0008		0.5488	0.5477	0.0020
	1.0000	0.4864	0.4859	0.0010		0.5576	0.5561	0.0027
	0.0000	0.4132	0.4117	0.0037		0.5218	0.5201	0.0032
	0.0588	0.4125	0.4076	0.0120		0.5112	0.5074	0.0074
	0.1232	0.4144	0.4099	0.0107		0.5023	0.4987	0.0070
	0.1942	0.4227	0.4170	0.0134		0.5042	0.5016	0.0052
	0.2726	0.4316	0.3814	0.1163		0.5108	0.4547	0.1099
300.15	0.3599	0.4418	0.4420	-0.0005	313.15	0.5216	0.5222	-0.0011
	0.4575	0.4595	0.4586	0.0020		0.5347	0.5346	0.0001
	0.5675	0.4702	0.4703	-0.0002		0.5460	0.5454	0.0011
	0.6922	0.4818	0.4807	0.0023		0.5574	0.5552	0.0038
	0.8350	0.4875	0.4882	-0.0015		0.5676	0.5668	0.0013
	1.0000	0.4972	0.4962	0.0020		0.5774	0.5770	0.0007
	0.0000	0.4368	0.4365	0.0006				
	0.0588	0.4323	0.4303	0.0047				
	0.1232	0.4339	0.4312	0.0062				
	0.1942	0.4381	0.4373	0.0019				
	0.2726	0.4486	0.3986	0.1112				
303.15	0.3599	0.4607	0.4604	0.0005				
	0.4575	0.4763	0.4759	0.0008				
	0.5675	0.4882	0.4877	0.0009				
	0.6922	0.4990	0.4983	0.0014				
	0.8350	0.5064	0.5054	0.0020				
	1.0000	0.5123	0.5127	-0.0008				

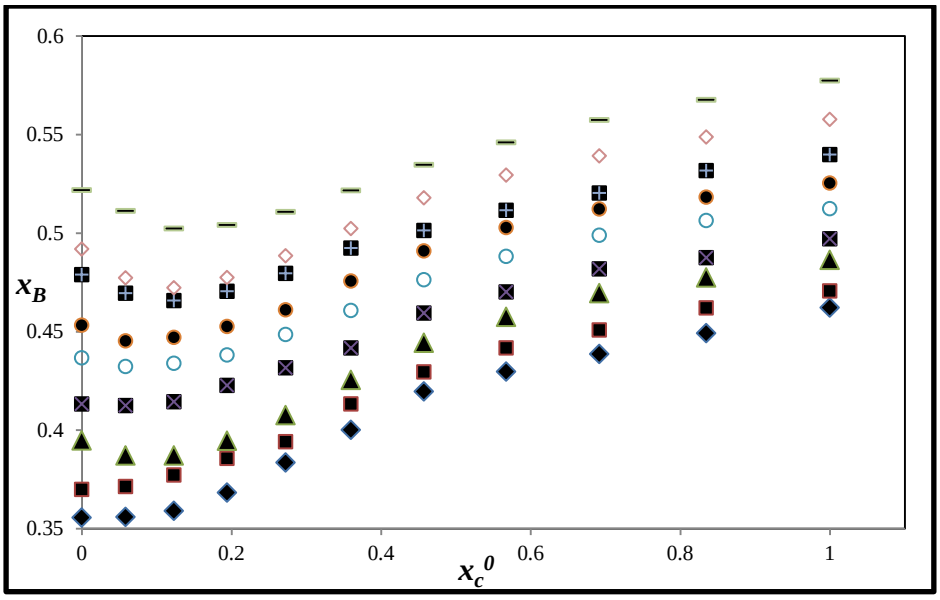


Figure 1. Mole fraction solubility (x_B) variation with initial mole fraction (x_C^0) of methanol at temperatures (◆ T=293.15 K, ■T=295.15 K; ▲T=298.15K; ×T=300.15 K; ○T=303.15 K; ●T=305.15 K; +T=308.15 K; ◇T=310.15 K & ▬T=313.15 K).

III. RESULTS AND DISCUSSION

Solubility

Table 1 show the experimental and calculated (using apelblat equation) values of solubility (x_B) of imidazole at 293.15 to 313.15 K in water + methanol. Variation of solubility with x_C^0 is visually shown in Figure 1.

The solubility of imidazole increases with temperature. Imidazole is an organic compound; naturally the solubility is more in organic solvents as compared with water, solubility of imidazole increase with increasing dielectric constant and dipole moment of organic solvent. In mixed solvents with water as the proportion of organic solvent increases, as expected the solubility also increases.

Apelblat model

Between the different methods, the modified semi-empirical Apelblat model is a suitable way to correlate solubility data against temperature [9, 10]. The equation is based on solid-liquid equilibrium theory provide excellent agreement between experimental and calculated values of solubility [11].

$$lnx_{B=} A + \frac{B}{T} + ClnT \quad (1)$$

A, B and C are the model parameters and T is temperature in Kelvin. A and B represent the non-idealities of the solutions in terms of the variation of activity coefficients, C reflects to the effect of temperature on the enthalpy of fusion [12]. A, B and C parameters were determined using non-linear least square fitting [13]. Solubility values of imidazole in water, methanol and in their water mixtures were calculated by equation (1). Relative deviation (RD) [14] was calculated using equation (2).

$$RD = \frac{x_B^{exp.} - x_B^{cal.}}{x_B^{exp.}} \quad (2)$$

From table 1, it can be seen that there is an excellent agreement between experimental and calculated values of mole fraction solubility. The values of parameters A, B, C along with co-relation coefficient (R^2) are listed in table 2. The relative deviations of experimental and calculated x_B are listed in table 1.

Table 2: Parameters and correlation errors of experimental values with the Apelblat equation

Solvents	x_C^0	Parameters			R^2
		A	B	C	
Methanol	0.0000	119.7162	-6930.51	-17.0948	0.9994
	0.0588	84.6615	-5243.46	-11.9366	0.9946
	0.1232	162.7293	-8660.34	-23.6257	0.9904
	0.1942	147.0913	-7876.6	-21.339	0.9901
	0.2726	103.2558	-5828.35	-14.8663	0.9942
	0.3599	48.16114	-3253.82	-6.68565	0.9975
	0.4575	27.12025	-2213.12	-3.59844	0.9972
	0.5675	46.07719	-3043.15	-6.43251	0.997
	0.6922	65.59265	-3906.66	-9.34551	0.9958
	0.8350	-37.8384	777.1498	6.05374	0.9985
	1.0000	-130.269	4981.286	19.8048	0.9988

NIBS-Redlich-Kister model

The solubility data at constant temperature is fitted into combined NIBS-Redlich-Kister model [15-18].

$$lnx_B = x_C^0 lnx_1 + x_A^0 lnx_2 + x_C^0 x_A^0 \sum_{i=0}^{3} M_i \, (x_C^0 - x_A^0)^i \quad (3)$$

Where x_A^0 is initial mole fraction of water and x_1 and x_2 are solubilities of imidazole in pure methanol and water, respectively. M_i is curve fit parameters (four parameter equation). All values of M_i along with R^2 value are listed in table 3. The values of R^2 are close to unity shows that NIBS-Redlich-Kister model is very well applicable for this solubility data.

Table 3. Values of Coefficients of NIBS-Radlich-Kister Equations

T/K	Range of x_C^0	M_0	M_1	M_2	M_3	R^2
imidazole + water + methanol						
293.15	0.058-0.834	0.162	0.138	-0.388	4.323	0.977
295.15	0.058-0.834	0.147	0.142	-0.238	3.180	0.975
298.15	0.058-0.834	0.102	0.247	-0.456	0.168	0.999
300.15	0.058-0.834	8.804	0.175	-0.250	-4.379	0.989
303.15	0.058-0.834	6.429	0.203	-0.250	5.898	0.997
305.15	0.058-0.834	6.320	0.171	-0.328	0.164	0.994
308.15	0.058-0.834	-2.077	0.141	-0.256	0.231	0.995
310.15	0.058-0.834	-9.196	0.208	-0.396	0.266	0.999
313.15	0.058-0.834	-7.437	0.284	-0.261	-3.104	0.987

Thermodynamics functions of dissolution

According to the van't Hoff equation, the standard molar enthalpy change of solution ΔH^0_{soln} is generally obtained from the slope of the $\ln x_B$ versus 1/T plot. Average temperature T_{hm} is introduced to obtain a single value of ΔG^0_{soln} and ΔS^0_{soln} in the temperature range studied

$$T_{hm} = \frac{n}{\sum_{i=1}^{n}\left(\frac{1}{T}\right)} \quad (4)$$

Where n is the number of experimental points. In the present work, T_{hm} = 302.92 K and the temperature range is (293.15 to 313.15) K in both pure solvents and binary solvent mixtures. Values of ΔH^0_{soln} are derived using equation 5.

$$\Delta H^0_{sol} = -R\left(\frac{\partial ln x_B}{\partial 1/T}\right) = -R\left[\frac{\partial ln x_B}{\partial\left(\frac{1}{T}-\frac{1}{T_{hm}}\right)}\right] \quad (5)$$

The lnx_B versus $(1/T - 1/T_{hm})$ plot of different solutions including pure solvents and binary solvent mixtures are displayed in Figures 2. From these figures, it can be seen that a trend of increasing solubility with temperature is observed. The slope and the intercept for each solvent are listed in Table 4. Thus the modified van't Hoff equation can be thought to be fit to calculate the enthalpy change of solution. The standard molar Gibbs energy change for the solution process ΔG^0_{soln}, can be calculated in the way similar to Krug et al [19] as

$$\Delta G^0_{sol} = -RT_{hm} \times intercept \quad (6)$$

In which the intercept used, is that obtained in plots of lnx_B as a function of $(1/T - 1/T_{hm})$. The standard molar entropy change ΔS^0_{soln} is obtained from

$$\Delta S^0_{Sol} = \frac{(\Delta H^0_{Sol} - \Delta G^0_{sol})}{T_{hm}} \quad (7)$$

Both ΔG^0_{soln} and ΔS^0_{soln} pertain to the mean temperature T_{hm} = 302.92 K. The results are shown in table 5, along with relative contribution of enthalpy (ζH) and entropy (ζTS) given by equation 8 and 9 respectively [20].

$$\zeta_H = \frac{|\Delta H^0_{Sol}|}{(|\Delta H^0_{Sol}| + |T\Delta S^0_{Sol}|)} \quad (8)$$

$$\zeta_{TS} = \frac{|T\Delta S^0_{Sol}|}{(|\Delta H^0_{Sol}| + |T\Delta S^0_{Sol}|)} \quad (9)$$

The values of ΔH^0 and ΔS^0 for all solutions are positive indicating the solution process as endothermic. The contribution of enthalpy to positive molar Gibbs energy is more as compared to entropy for solutions.

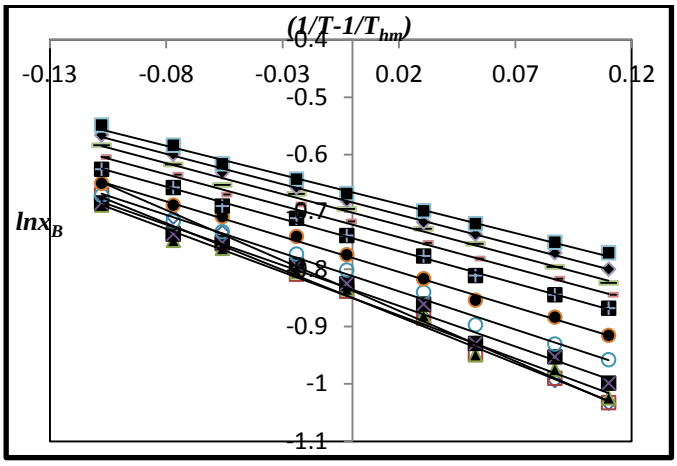


Figure 2. Plot of lnx_B versus $(1/T - 1/T_{hm})$ for imidazole + water + methanol system with initial mole fraction (◇ x^0_C=0.0000; □ x^0_C=0.0588; ▲ x^0_C=0.1232; x x^0_C=0.1942; ○ x^0_C=0.2726; ● x^0_C=0.3599; + x^0_C=0.4575; - x^0_C=0.5675; ▬ x^0_C=0.6922 & ◆ x^0_C=0.8350; ■ x^0_C=1.0000).

Table 4. Slope (m) and intercept (c) of the lnx_B versus $(1/T - 1/T_{hm})$ plot along with R^2

x^0_C	m	c	R^2
0.0000	-1754	-0.837	0.998
0.0588	-1629	-0.850	0.994
0.1232	-1506	-0.850	0.988
0.1942	-1415	-0.835	0.988
0.2726	-1333	-0.812	0.993
0.3599	-1229	-0.780	0.997
0.4575	-1123	-0.746	0.997
0.5675	-1095	-0.722	0.996
0.6922	-1076	-0.701	0.995
0.8350	-1055	-0.683	0.998
1.0000	-1015	-0.665	0.995

Table 5: Thermodynamic functions relative to solution process of imidazole at T_{hm} = 302.92 K

x_C^0	ΔH_{sol}^0/kJ ·K^{-1}· mol^{-1}	ΔG_{sol}^0/kJ ·K^{-1}· mol^{-1}	ΔS_{sol}^0/kJ ·K^{-1}· mol^{-1}	$T\Delta S_{sol}^0$/kJ ·K^{-1}· mol^{-1}	ζH	ζTS
0.0000	14.5828	2.1080	0.0412	12.4747	53.8954	46.1046
0.0588	13.5435	2.1408	0.0376	11.4028	54.2908	45.7092
0.1232	12.5209	2.1408	0.0343	10.3801	54.6739	45.3261
0.1942	11.7643	2.1030	0.0319	9.6613	54.9076	45.0924
0.2726	11.0826	2.0450	0.0298	9.0375	55.0821	44.9179
0.3599	10.2179	1.9645	0.0272	8.2534	55.3176	44.6824
0.4575	9.3366	1.8788	0.0246	7.4578	55.5936	44.4064
0.5675	9.1038	1.8184	0.0240	7.2854	55.5475	44.4525
0.6922	8.9459	1.7655	0.0237	7.1804	55.4740	44.5260
0.8350	8.7713	1.7202	0.0233	7.0511	55.4359	44.5641
1.0000	8.4387	1.6748	0.0223	6.7639	55.5084	44.4916

IV. CONCLUSION

This paper reports experimental data for the solubility of imidazole in pure water, methanol and binary mixtures of water-methanol from (293.15-313.15) K. the solubility of imidazole was found to increase with increase in temperature. The thermodynamic aspects of the solubility process of imidazole in binary mixtures were studied in order to select the best solvent and optimize its solubility.

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VI. REFERENCES

[1]. Kale S.S., Pawar R.R., Kale A.S., 2016, Imidazole, its derivatives & their importance: a review. International Journal of Current Advanced Research, 5(5): 906-911.

[2]. Chawla A., Sharma A., Sharma A.K., 2012, review: a convenient approach for the synthesis of imidazole derivatives using microwaves. scholars research library, der pharma chemical. 4(1): 116-140.

[3]. Fathi-Azarjbayjani A., Mabhoot A., Martinez F., 2016, Modeling, solubility and thermodynamic aspects of sodium phenytoin in propylene glycol-water mixtures, Journal of molecular liquids. 219: 68-73.

[4]. Domanska Urszula, Kozlowska Marta, 2002, Solubility of Imidazoles in Alcohols. J. Chem. Eng. Data, 47: 8-16.

[5]. Domanska Urszula, Kozlowska Marta, 2003, Solubility of imidazoles in ethers. J. Chem. Eng. Data, 48: 557-563.

[6]. Pawar R.R., Aher C.S., Pagar J.D., 2012, Solubility, density and solution thermodynamics of NaI in different pure solvents and binary mixtures. J. Chem. Eng. Data, 57: 3563-3572.

[7]. Pawar R.R., Nahire S.B., Hasan M., 2009, Solubility and density of potsium iodide in binary water ethanol solvent mixtures at (298.15, 303.15, 308.15, and 313.15) K. J. Chem. Eng. Data, 54: 1935–37.

[8]. Pawar R.R., Golait S.M., Hasan M., 2010, Solubility and density of potsium iodide in binary water-propan-1-ol solvent mixtures at (298.15,303.15, 308.15 and313.15)K. J. Chem. Eng. Data, 55: 1314–16.

[9]. Lourenço C., Melo C.I., Bogel-Łukasik R., 2012, J. Chem. Eng. Data, 57: 1525–1533.

[10]. Melo C.I., Bogel-Łukasik R., Nunes da Ponte M., 2013, Fluid Phase Equilib., 338: 209–216.

[11]. Domanska U., Bogel-Łukasik R., 2005, J. Phys. Chem. B., 109: 12124–12132.

[12]. Apelblat A., Manzurola, 1999, E. J. Chem. Thermodyn., 31: 85–91.

[13]. Gans P., Sabatini A., Vacca., 1996, Investigation of equilibria in solution. Determination of equilibrium constants with hyperquad suite of program, Talanta., 43: 1739–1753.

[14]. Guo H., Song L., Zhu C., 2016, Measurement and correlation of solubility of pronamide in five organic solvents at (278.15-323.15) K. J. Chem. Thermodynamics, 99: 11-15.

[15]. Jouyban A., Khoubnasabjafari M., Chan H., 2002, Solubility prediction of anthracene in mixed solvents using a minimum number of experimental data. Chem. Pharm. Bull., 50: 25–25.

[16]. Joyce R., Powell B., Miller J., 1995, Solubility of Anthracene in binary alcohol + 1,4-dioxane solvent mixtures. J. Chem. Eng. Data, 40: 1124–1126.

[17]. Acree W.E., Zvaigzne A.I., 1991, Thermodynamic properties of nonelectrolyte solutions: part 4. estimation and mathematical representation of solute activity coefficients and solubilities in binary solvents using the NIBS and modified Wilson equations. Thermochim. Acta, 178: 151–167.

[18]. Acree W.E., 1992, Jr. Mathematical representation of thermodynamic properties: Part 2. Derivation of combined nearly ideal binary solvents NIBS/Redlich-Kister mathematical representation from a two body and three body interactional mixing model. Thermochim. Acta, 198: 71–79.

[19]. Krug R.R., Hunter W.G., Grieger R.A., 1976, Enthalpy-Entropy Compensation. 2. Separation of the Chemical from the Statistical Effect. J. Phys. Chem., 80: 2341–2351.

[20]. Cui Z.P., Yin Q., Gong J., 2013, Fluid Phase Equilib., 337: 354-362.