Dissolution Enthalpies and Entropies of Potassium Fluoride in N,N-Dimethylacetamide, Diethanolamine, Sulfolane, Pyridine at 300-367 K

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The solubilities of potassium fluoride in different non-proton polar solvents had been determined using a dynamic method at temperature ranging from 300.87 to 367.37 K. The two parameters solubility equation was correlated with the experimental data. The dissolution enthalpy and dissolution entropy had been calculated from the solubility data. The interactions between solute and solvent were discussed. It provided the basic data for preparation of 2,3,4,5-tetrafluorobenzoic acid.

Keywords: Solubilities, Potassium fluoride, Non-proton polar solvents, N,N-Dimethylacetamide, Diethanolamine, Sulfolane.

INTRODUCTION

2,3,4,5-Tetrafluorobenzoic acid is an important pharmaceutical intermediate, commonly used in preparation of antibacterial agents of quinolone, such as lomefloxacin, sparfloxacin, fleroxacin, ofloxacin, levofloxacin and rufloxacin *etc.* which is characterized by broad-spectrum antimicrobial activity, high-effective and low cytotoxicity to human. Quinolone drug is clinically recognized to be a powerful and safe weapon for the treatment of various bacterial infections and has become a blockbuster drug, with annual sales of around 3 billion dollars worldwide. In the halogen-exchange fluorination reaction for preparation of 2,3,4,5-tetrafluorobenzoic acid, potassium fluoride is the commonly adopted raw materials[1]. Because the element fluorine has extreme electronegativity, the fluorination reaction must be carried out in non-proton polarity solvent under anhydrous condition to prevent the side reactions such as fluorine hydrolysis *etc.* In liquid-solid heterogeneous fluorination reaction, the solubilities of potassium fluoride in the non-proton polar solvents have great effect on the rate of fluorination reaction[2]. Therefore, in order to increase the rate of fluorination reaction, it is necessary to know the solubilities of potassium fluoride in the solvents and thermodynamic parameters. Based on the solubilities of potassium fluoride (KF) in N,N-dimethylacetamide (DMAC), diethanolamine, sulfolane, pyridine at temperatures ranging from 300.87 to 359.50 K[3], the solubility data were correlated by two parameters solubility equation and the dissolution enthalpy and dissolution entropy had been calculated from the solubility

data, and the solubilities correlated by two parameters solubility equation showed good agreement with the experimental data.

EXPERIMENTAL

Potassium fluoride, N,N-dimethylacetamide, diethanolamine, sulfolane, pyridine were all of AR grade, and they were obtained from Shanghai Chemical Reagent Co. and have mass fraction purities of 0.995.

Solubility measurements: The solubilities of potassium fluoride in N,N-dimethylacetamide, diethanolamine, sulfolane, pyridine were measured by a dynamic method described previously[4]. The uncertainty of temperature was ± 0.02 K.

The solubility expressed by the mole fraction was calculated as follows[5]:

$$x = \frac{m_1 / M_1}{m_1 / M_1 + m_2 / M_2} \tag{1}$$

where m_1 and m_2 represent the mass of the solute and the solvent. M_1 and M_2 are the molecular mass of the solute and the solvent.

To prove the feasibility and the uncertainty of the measurement, the solubility of KF in water were measured and compared with the values reported in the literature[6]. The experimental measurements agreed with the reported values with a mean relative deviation of 0.23 %.

RESULTS AND DISCUSSION

The solubility data of potassium fluoride in the non-proton polar solvents at different temperatures are listed in Table-1.

The temperature dependence of solubility for potassium fluoride in the different solvents is described by the two parameters solubility equation[7,8]:

$$\ln x = A + \frac{B}{T/K} \qquad (2)$$

where x is the mole fraction solubility of potassium fluoride, T is the absolute temperature, and A, B are the model parameters, the adjustable parameters A, B can be obtained from simple optimization.

The objective function $F = \min \sum \left| x_{ci} - x_i \right|^2$, the values of parameters A, B are listed in Table-2.

The calculated solubility x_c of potassium fluoride is given in Table-1.

The relative deviations between the experimental value and calculated value are also listed in Table-1. Relative deviations (RD) are calculated according to:

$$\text{Relative deviations} = \frac{x - x_c}{x} \qquad (3)$$

The relative average deviations (RAD) by equations are listed in Table-2. The relative average deviations is defined as

$$\text{Relative average deviations} = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{x_i - x_{ci}}{x_i}\right| \qquad (4)$$

The relative deviations are listed in Table-1. And the model parameters and relative average deviations are listed in Table-2.

From Table-2, it can be found that the calculated solubilities show good agreement with the experimental data. The relative average deviations are 1.60, 1.40, 1.89 and 2.12 %, respectively, which indicates that the two parameters equation is suitable to correlate the solubility data of potassium fluoride in these non-proton polar solvents.

By using the data shown in Table-1, the solubility curves for the studied systems by two parameters equation are plotted in Fig. 1, it is evident that the solubility of each system is low. The solubility data of potassium fluoride in N,N-dimethyl acetamide, diethanolamine, sulfolane, pyridine showed a flat uptrend when the temperature increased.
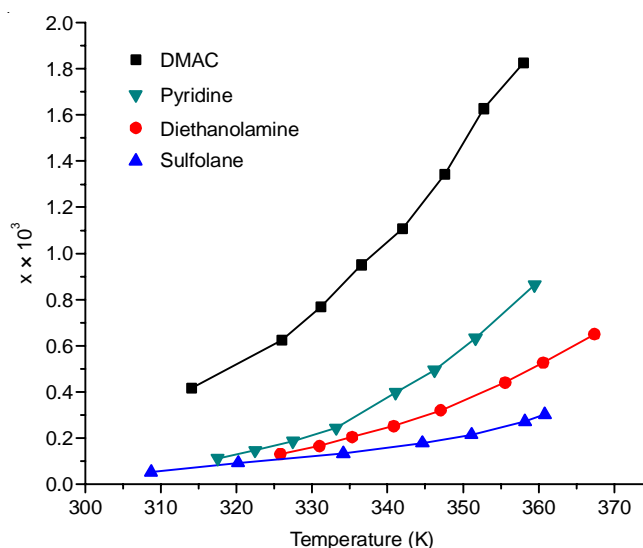

Fig. 1. Solubility of potassium fluoride in N,N-dimethylacetamide, diethanolamine, sulfolane and pyridine

TABLE-1
SOLUBILITIES OF POTASSIUM FLUORIDE IN N,N-DIMETHYLACETAMIDE, DIETHANOLAMINE, SULFOLANE AND PYRIDINE

T (K)	10^3x	10^3x_c	100 Relative deviation	T (K)	10^3x	10^3x_c	100 Relative deviation
N,N-Dimethylacetamide				Diethanolamine			
314.06	0.4153	0.4087	1.59	325.81	0.1300	0.1331	-2.38
325.98	0.6236	0.6406	-2.73	330.99	0.1646	0.1662	-1.01
331.19	0.7681	0.7745	-0.83	335.31	0.2044	0.1991	2.59
336.57	0.9498	0.9328	1.79	340.85	0.2516	0.2492	0.94
342.02	1.107	1.119	-1.08	347.03	0.3203	0.3174	0.88
347.57	1.342	1.342	0.00	355.56	0.4404	0.4373	0.71
352.79	1.628	1.579	3.01	360.59	0.5266	0.5244	0.41
358.00	1.826	1.859	-1.81	367.37	0.6498	0.6647	-2.29
Sulfolane				Pyridine			
308.73	0.05190	0.05203	-0.25	317.52	0.1117	0.1095	1.94
320.21	0.09189	0.08928	2.84	322.50	0.1461	0.1444	1.17
334.16	0.1325	0.1326	-0.07	327.48	0.1853	0.1892	-2.13
344.66	0.1780	0.1835	-3.12	333.17	0.2434	0.2567	-5.49
351.13	0.2140	0.2221	-3.79	341.10	0.3973	0.3820	3.86
358.20	0.2711	0.2714	-0.12	346.26	0.4946	0.4921	0.51
360.85	0.3012	0.2920	3.04	351.67	0.6326	0.6340	-0.21
–	–	–	–	359.49	0.8640	0.8783	-1.66

TABLE-2
PARAMETERS OF POTASSIUM FLUORIDE IN N,N-DIMETHYLACETAMIDE, DIETHANOLAMINE, SULFOLANE AND PYRIDINE

Solvent	A	B	R^2	10^2 Relative average deviations
N,N-Dimethylacetamide	4.5314	-3873.7	0.9985	1.60
Diethanolamine	5.2918	-4631.8	0.9991	1.40
Sulfolane	1.7472	-3567.3	0.9931	1.89
Pyridine	9.0079	-5756.5	0.9979	2.12

TABLE-3
Δ_{sol}H AND Δ_{sol}S FOR POTASSIUM FLUORIDE IN DIFFERENT SOLVENTS AT DIFFERENT TEMPERATURES

T (K)	Δ_{sol}H (kJ mol⁻¹)	Δ_{sol}S (J mol⁻¹ K⁻¹)	T (K)	Δ_{sol}H (kJ mol⁻¹)	Δ_{sol}S (J mol⁻¹ K⁻¹)
N,N-Dimethylacetamide (DMAC)			Sulfolane		
314.06	32.20	102.55	308.73	29.66	96.07
325.98	32.20	98.80	320.21	29.66	92.62
331.19	32.20	97.24	334.16	29.66	88.75
336.57	32.20	95.69	344.66	29.66	86.05
342.02	32.20	94.16	351.13	29.66	84.46
347.57	32.20	92.66	358.20	29.66	82.80
352.79	32.20	91.29	360.85	29.66	82.19
358.00	32.20	89.96	–	–	–
Diethanolamine			Pyridine		
325.81	38.51	118.19	317.52	47.86	150.73
330.99	38.51	116.34	322.50	47.86	148.40
335.31	38.51	114.84	327.48	47.86	146.14
340.85	38.51	112.98	333.17	47.86	143.65
347.03	38.51	110.97	341.10	47.86	140.31
355.56	38.51	108.30	346.26	47.86	138.22
360.59	38.51	106.79	351.67	47.86	136.09
367.37	38.51	104.82	359.49	47.86	133.13

According to molecular thermodynamics of fluid-phase equilibrium, referring to the method of Tong and other[7,8]. The solvent can be treated as a pseudo solvent. Referring to the study of Saraswat et al.[9,10], the activity coefficient of potassium fluoride in the potassium fluoride phase and the activity coefficient of the solvent in the solvent phase both are assumed as 1. Within the limited range of studied temperatures and solubilities, dissolution enthalpies Δ_{sol}H and dissolution entropies Δ_{sol}S for potassium fluoride in solvent can be derived as follows:

$$\Delta_{sol}H = RT^2 \left(\frac{\partial \ln x}{\partial T}\right)_p \tag{5}$$

$$\Delta_{sol}S = RT \left(\frac{\partial \ln x}{\partial T}\right)_p \tag{6}$$

Differentiating eqn. 2 and collating it into eqns. 5 and 6, the following equations can be obtained

$$\Delta_{sol}H = -RB \tag{7}$$

$$\Delta_{sol}S = -RB/T \tag{8}$$

According to parameters of the two parameters solubility equation listed in Table-2, Δ_{sol}H and Δ_{sol}S listed in Table-3 can be calculated from eqns. 7 and 8, respectively.

From Table-3, it is found that the course of potassium fluoride dissolving in each solvent in the experimental temperature range was endothermic, Δ_{sol}H > 0 and Δ_{sol}S for potassium fluoride dissolving in each solvent was relatively large. The positive Δ_{sol}H and Δ_{sol}S for potassium fluoride revealed that potassium fluoride being dissolved in each solvent was an entropy-driving process. This phenomenon likely resulted from the different molecular structures and space conformations between the solute and the solvent. Solvent molecules selected for the present study are strong association complexes with small molecular dimension[10]. Owing to the solute molecules containing characteristics groups -F, perhaps the dissolution process of such a solute in solvents involves some forces such as solvent polarization, electrostatic, hydrogen bond, hydrophobic interaction, solvent-based, stereoscopic effect, etc. For the entropy-driving process, the reason for the entropy increase during the dissolution process is that the solutes disrupt the alignment of the solvent molecules and therefore reduced the degree of order of the system while they were dissolved in various solvents. The endothermic effect in the dissolving process (Δ_{sol}H > 0) is perhaps because the interactions between potassium fluoride molecules and the solvent molecules are more powerful than those between the solvent molecules; the newly formed bond energy between potassium fluoride molecule and the solvent molecule is not powerful enough to compensate the energy needed for breaking the original association bond in the various solvents, and the system needs to absorb heat from surroundings and manifests as increasing enthalpy.

Conclusion

Based the solubilities of potassium fluoride in N,N-dimethylacetamide, diethanolamine, sulfolane, pyridine, the two parameters solubility equation was correlated with the experimental data, and the dissolution enthalpies Δ_{sol}H and dissolution entropies Δ_{sol}S were estimated. The overall relative average deviations is 1.75×10^{-2}. The calculated results show good agreement with the experimental data. The positive Δ_{sol}H and Δ_{sol}S indicates that the dissolution process of potassium fluoride in the system was an entropy-driven process.

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