Experimental and Theoretical Studies of Thermodynamics of Lithium Chloride in methanol

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Introduction

Thermodynamic properties of the non aqueous binary electrolyte solutions are useful in prediction of behavior of electrolyte systems, development of models for electrolytes in solutions and estimation of the interactions occurring in these solutions [1-7].

In the present work we have determined the activity and the activity coefficient of both solute and solvent in the concentration range of \(0.01-2\) mol.kg\(^{-1}\) through the measurement of the vapor pressure of methanol above the solutions, using Head-Space Gas Chromatographic technique (HS-GC) and have also calculated all the related thermodynamic properties [8, 9].

Experimetal

The salts (LiX,X:Cl,Br and I) and methanol were obtained from Merck.

They were all supra pure reagents, (LiX,GR, min. 99.5% ;absolute methanol GR, min . 99.8% ). All measurements were carried out by using a Shimadzu model 16 A gas chromatograph equipped with FID detector and a column loaded with 15% diethyleneglycol succinate (DEGS) supported on shimalite . Solutions of LiX in methanol were prepared and thermostatted (25±0.01 \(^{\circ}\)C). Samples (0.3 ml) of the head –space above the solutions were taken using a 1 ml gas-tight syringe (Hamilton) and injected into the gas chromatograph. Due care has to be taken in removing the exact sample and injecting it to the gas chromatograph. Usually 5 samples with half an hour of interval time (time necessary for equilibrium to be established between the gas phase
and liquid phase) were injected and the average values of the area peaks were calculated and taken as detector response.

Results and Discussion

Tables 1-3 shows all the measurements and results which have been obtained in this work. The values of vapor pressure of methanol above the solutions are listed in third column. All measurements were made five times and the activity coefficients of the methanol were calculated.

Figure 1. shows the osmotic coefficient of various solution of different concentration of LiCl in methanol which indicates the possibility of obtaining the osmotic coefficient of very diluted methanol solutions which are not be possible by other methods such as isopiestic method.

Figure 2. shows the excess free energies of the different solutions of LiCl in methanol. This should be noted that this has not been previously reported in the literature, because to determine the thermodynamics quantities of these solutions one needs to have the value of osmotic coefficient of much diluted solution (i.e. $10^{-4}$ mol.kg$^{-1}$).

![Figure 1. The osmotic coefficient of LiCl methanol solutions](image1)

![Figure 2. Excess Gibbs free energy of LiCl solutions in methanol at 298.15K.](image2)
REFERENCES
