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Consistency of experimental data in SLLV equilibrium of ternary systems with electrolyte. Application to the water + NaCl + 2-propanol system at 101.3 kPa

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ABSTRACT

The SLLV phase equilibria of the water + NaCl + 2-propanol mixture have been determined experimentally at 101.3 kPa by means of a modified recirculating still. The results obtained allow us to study the shape of the phase diagram of the system, to analyze the evolution with temperature of this equilibrium diagram and to show the differences with a similar system such as water + NaCl + 1-propanol.

Moreover, the experimental data obtained have been compared with previously published data showing their important inconsistencies and presenting the rules that must be met by the experimental equilibrium data of water + non-volatile salt + organic solvent type systems in each one of the different SLLV, LLV and SLV equilibrium regions.

1. Introduction

The knowledge of the equilibrium phase diagram of mixed solvent electrolyte systems is important because this type of mixture is found in many processes. These processes include regeneration of solvents, liquid-liquid extraction of mixtures containing salts and extractive distillation and crystallization. For example, the salt effect distillation is used commercially in the concentration of aqueous nitric acid, using the salt magnesium nitrate as the separating agent. Other commercial applications include acetone-methanol separation using calcium chloride and isopropanol-water separation using the same salt [1].

However, the literature available on the mixed solvent electrolyte systems is scarce. Moreover, the relatively small amount of existing experimental data is incomplete and some of them containing important inconsistencies as shown in a previous paper [2].

Finally, the thermodynamic models used to represent these systems, such as the extended UNIQUAC model for electrolytes [3], or the electrolyte NRTL model [4] all need the equilibrium data to calculate the model parameters.

In two previous papers [2,5], we studied the equilibrium diagram of the water + NaCl + 1-butanol and water + NaCl + 1-propanol systems at 101.3 kPa in order to examine the shapes of the various equilibrium surfaces and regions that occur in them. To do this, a detailed analysis of the evolution with temperature of the different equilibrium regions of these systems was carried out. The influence of salt on the equilibrium was investigated demonstrating that many of the previously published data were inconsistent and inaccurate. It is really important to have reliable experimental data suitable for the development of new thermodynamic models or obtaining new binary interaction parameters with the existing models.

In the previously studied systems, the electrolyte was NaCl although there was an important difference between them: the 1-butanol is partly miscible with water while 1-propanol is completely miscible. The objective of the present paper is to extend those studies with NaCl to another system involving a completely miscible solvent in order to verify the inconsistency of previously published data and to analyze once again the evolution with temperature of the different equilibrium regions. The chosen system is water + NaCl + 2-propanol at 101.3 kPa whose equilibrium phase diagram could be in principle similar to that with 1-propanol since both systems contain a binary water + propanol with a homogeneous minimum boiling azeotrope. However, as shown in Fig. 1, the azeotropic composition of the two systems is quite different: 0.69 mol fraction in 2-propanol [6,7] for one of them and 0.43 in 1-propanol [8,9] for the other one. This fact could make the phase

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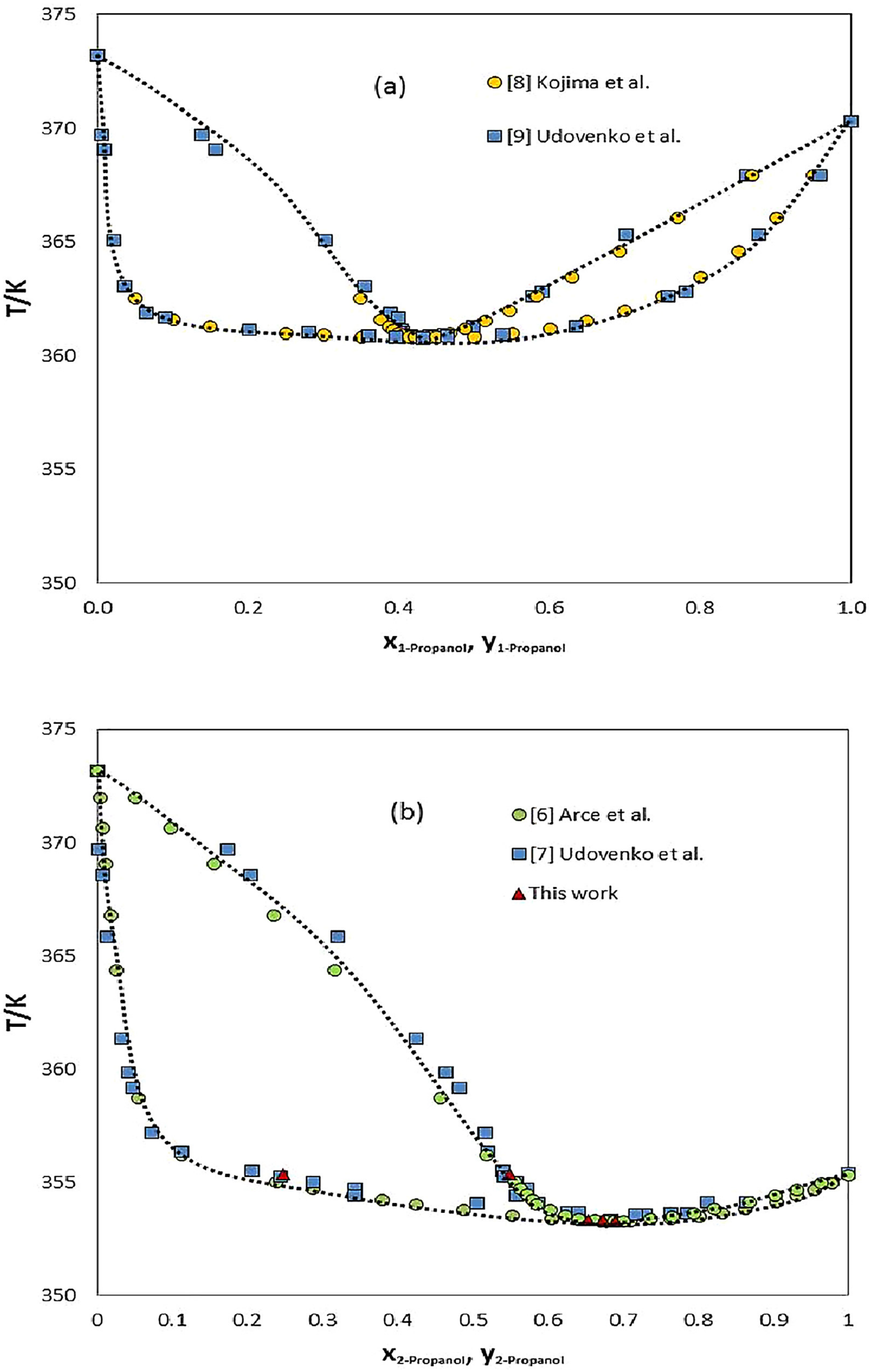

Fig. 1. Binary equilibrium diagrams. a). Txy of water + 1-propanol at 101.3 kPa. b). Txy of water + 2-propanol at 101.3 kPa. Compositions in mole fraction.

diagrams of both systems and their evolution with the temperature very different.

In this work, LV (liquid-vapor), LLV (liquid-liquid-vapor), SLV (solid-liquid-vapor) and SLLV (solid-liquid-liquid-vapor) equilibrium data of the water + NaCl + 2-propanol system at 101.3 kPa have been determined experimentally. The results obtained permit us to carry out a study of the shape of the phase diagram of the system, to show the inconsistency of previous