بنام خداوند جان و خرد

IN THE NAME OF GOD

THERMODYNAMIC PROPERTIES OF NON ELECTROLYTE BINARY SOLUTIONS

Excess Enthalpy, Excess Volume,

Correlations and Thermodynamic Models

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BY

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Under Supervision of

Dr. HOSSEIN ILOUKHANI

Dr. MOHAMAD SOLTANIEH

THESIS

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LIST OF PUBLISHED PAPERS:

1- **H. Iloukhani and J. B. Parsa .** Enthalpies of Mixing for The Binary Mixtures of Tetrachloroethylene With Some Alkan-1-ols (C_3-C_8) at 298.15 K. Phys.Chem. Liq.36,141-147, 1998.

2- **H. Iloukhani and J.B. Parsa and A. A. Sabouri.** Excess Molar Enthalpies of Binary Mixtures Containing N,N-Dimethylformamide + Six 2- Alkanols (C_3-C_8) at 300.15 K. J. Chem. Eng. Data.45(6),1016-1018, 2000.

3- **H. Iloukhani and J. B. Parsa .** Excess Molar Enthalpies of Binary Mixtures Containing Trichloroethylene +Six 2-Alkanols (C_3-C_8) at 298.15 K. Accepted for Printing in J. Solution Chemistry. 30(5), 1, 2001.

4- **H. Iloukhani and J.B. Parsa and M. Soltanieh .** Excess Enthalpies Data in Some Binary Systems Containing Non electrolyte Solutions and Their Correlations at 298.15 K.Part I. Phys. Chem. Liq. In press, 2001.

5- **H. Iloukhani and J.B. Parsa and M. Soltanieh .** Excess Enthalpies Data in Some Binary Systems Containing Non electrolyte Solutions and Their Correlations at 298.15 K.Part II. Phys. Chem. Liq. In press, 2001.

6- **H. Iloukhani and J.B. Parsa and M. Soltanieh.** Volumetric Properties of Acetonitrile With 1,2-Alkandiols (C_2-C_6) at 293.15 K. Submitted .

Dedicated to:

Scientists, my parents, my wife
and my daughter, Shadi

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ABSTRACT

Ph.D. thesis by Jalal Basiri Parsa

Title: Thermodynamic properties of non-electrolyte binary solutions: excess enthalpy, excess volume, correlations and thermodynamic models

Keywords: Excess Properties, NRTL, Wilson, Redlich-Kister, Alkanols, Microcalorimeter, Dilatometer, Pycnometer .

Abstract: In this thesis thermodynamic properties of non-electrolyte binary solutions such as excess molar enthalpies, H_m^E and excess molar volumes, V_m^E have been measured and the resulted data were correlated to the mathematical and thermodynamic models.

Excess enthalpies of mixing for tetrachloroethylene + six 1-alkanols (C_3-C_8) at 298.15 *K*, trichloroethylene + six 2-alkanols (C_3-C_8) at 298.15 *K* and *N,N*-dimethyl formamide + six 2-alkanols (C_3-C_8) at 300.15 *K* were measured using microcalorimeter and the resulted data are fitted to the mathematical model "Redlich- Kister" equation:

$$H^E / J \cdot mol^{-1} = x(1-x)\sum_{k=1}^{N} A_k (1-2x)^{k-1}$$

And its parameters were calculated by means of least square method. The results are discussed in terms of self-association between unlike molecules. The observed negative excess molar enthalpies of mixing for the binary systems of tetrachloroethylene and 1-alkanols, indicate that the dissociation of the associated species of the 1-alkanols on dilution with tetrachloroethylene is the dominating force. Excess enthalpies vary little with the chain length of the 1-alkanols. Since 1-alkanols are strongly associated through hydrogen bonding, dilution with a non-polar solvent like

tetrachloroethylene results in changes in enthalpies of mixing. For trichloroethylene + six 2-alkanols all the studied mixtures exhibit exothermic effect and showed a minimum around 0.5-0.6 mole fraction of trichloroethylene. The results are explained in terms of strong self-association exhibited by 2-alkanols and cross-association of the O···HO specific interaction and the polarity of trichloroethylene.

Excess molar enthalpies of *N, N*-dimethylformamide + six 2-alkanols (C_3–C_8), show positive values over the entire ranges of composition and increase based on the number of carbon atoms in each molecule of 2-alkanols. The results are explained in terms of strong self-association exhibited by the 2-alkanols and cross-association of O···HO specific interaction and the greater polarity of *N,N*-dimethylformamide.

In the next step the experimental data related to excess molar enthalpies for binary solution at 298.15 *K* including the following systems were collected from literature and the data correlated to two thermodynamic models NRTL and Wilson, respectively :

$$H^E = x_1 x_2 \left[\frac{\lambda_{12}\Lambda_{12}}{x_1 + \Lambda_{12}x_2} + \frac{\lambda_{21}\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right] \qquad \text{(Wilson)}$$

$$H^E = RT x_1 x_2 \left[\frac{\tau_{21}G_{21}(x_1 + x_2 G_{21} - x_1\alpha_{12}\tau_{21})}{(x_1 + x_2 G_{21})^2} + \frac{\tau_{12}G_{12}(x_2 + x_1 G_{12} - x_2\alpha_{12}\tau_{12})}{(G_{12}x_1 + x_2)^2} \right] \qquad \text{(NRTL)}$$

The literature data consist of :

i- Trichloroethylene + 2-alkanols

ii- Chlorohydrocarbon + hydrocarbons

iii- Ether + hydrocarbons

iv- Water + alkanolamines

v- Mono and polybromoalkanes

vi- Propylene carbonate + alkanoates

vii- Cyclic ether + hydrocarbons

For each system the parameters of the two models are calculated by using the experimental excess enthalpies and Newton-Raphson least square method . For the systems where relative deviation between calculated and experimental values are considerable, a modified NRTL model based on (α_{12}) parameter as a function of mole fraction (x) is suggested in this work.

In cases where excess enthalpies are not large and H_m^E *vs.* x curves are symmetric all tested models are able to fit experimental data with good accuracy. Among them the NRTL equation provides the best fit for such systems. However, when excess enthalpy curve is asymmetric the modified NRTL model proposed in this work performs better.

In the next section, for binary systems of acetonitrile + 1,2-alkanediols (C_2–C_6) the values of excess molar volumes at 298.15 K were measured and fitted to the mathematical model "Redlich-Kister" equation by means of least square method and its parameters were calculated. The values of excess partial molar volumes, $\overline{V}_i^E$ were calculated from excess molar volumes, V_m^E and the excess partial molar volumes have been extrapolated to zero concentration to obtain the limiting values of infinite dilution $\overline{V}_i^{E,0}$. V_m^E for acetonitrile + 1,2-ethanediol and 1,2-propanediol mixtures are negative and positive values are obtained for all remaining systems. The results are explained in terms of dissociation of the self - association 1,2 - alkandiols and the formation of the O-H···N≡C hydrogen bonding.

Excess partial molar volumes, $\overline{V}_i^E$ were also calculated from excess molar volumes by the following equations,

$$V^E = x(1-x)\sum_{k=1}^{N} A_k (1-2x)^{k-1}$$

$$\overline{V}_1^E = V^E + (1-x)\left(\frac{\partial V^E}{\partial x}\right)$$

$$\overline{V}_2^E = V^E - x\left(\frac{\partial V^E}{\partial x}\right)$$

in which V^E, $\overline{V}_1^E$ and $\overline{V}_2^E$ are excess molar volumes, excess partial molar volumes of acetonitrile and excess partial molar volumes of 1,2-alkanediols molecules respectively.

At infinite dilution the excess partial molar volumes for two components, $\overline{V}_i^{E,0}$ were calculated by,

$$\overline{V}_1^{E,0} = \sum_{k=1}^{N} A_k$$

$$\overline{V}_2^{E,0} = \sum_{k=1}^{N} A_k (-1)^{k-1}$$

in which $\overline{V}_1^{E,0}$ and $\overline{V}_2^{E,0}$ are the excess partial molar volume of acetonitrile at infinite dilution in 1,2-alkanediols and the excess partial molar volumes of 1,2-alkanediols at infinite dilution in acetonitrile, respectively, $\overline{V}_i^E$ are negative and increase over the whole range of acetonitrile concentration for 1,2-ethanediol and 1,2-propanediol mixtures and for remaining systems $\overline{V}_i^E$ are positive and decrease on the whole range of acetonitrile concentration.

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