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Excess enthalpies of oxygenated compounds + hydrocarbon mixtures: Binary and ternary mixtures containing dibutyl ether (DBE), 1-butanol and 2,2,4-trimethylpentane at 298.15 K

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ABSTRACT

Measurements of excess molar enthalpies at the temperature of 298.15 K and atmospheric pressure in a quasi-isothermal flow calorimeter are reported for the ternary system dibutyl ether (DBE) + 1-butanol + 2,2,4-trimethylpentane (TMP) and the corresponding binary systems. All the binary and the ternary systems show endothermic character. The Redlich–Kister equation and the NRTL and UNIQUAC models have been used to fit the experimental data for the binary and ternary systems.

1. Introduction

Presently several oxygenated compounds are added to gasoline to enhance the octane number and to reduce air pollution. For proper design of synthesis and separation processes of these reformulated gasolines, which contain ethers and alcohols, the phase behaviour and thermodynamic properties of the fluid mixtures need to be known. As a part of our research work on thermodynamic properties of octane boosters [1,2], this paper presents experimental excess molar enthalpies of the ternary system DBE + 1-butanol + 2,2,4-trimethylpentane and the corresponding binary systems at $T = 298.15$ K and atmospheric pressure. DBE is used as blending agent in reformulated gasoline and 1-butanol is a basic component in the synthesis of the ether, and therefore is always contained as an impurity. 2,2,4-Trimethylpentane is an essential component in gasoline. Excess molar enthalpies have been measured with a quasi-isothermal flow calorimeter. The experimental data have been fitted using polynomial equations and group contribution models. The values of the standard deviation indicate good agreement between the experimental results and those calculated from the equations. Data are also used to describe the structural effects and interactions that occur between molecules in the solutions.

2. Experimental

All the chemicals used here were purchased from Fluka Chemie AG and were of the highest purity available, chromatography quality reagents (of the series puriss p.a.) with a stated purity >99.5%. The purity of all reagents was checked by gas chromatography, and the values of purity obtained were >99.6% for DBE, >99.8% for TMP and >99.8% for 1-butanol. The water content of 1-butanol was checked to be less than 0.009%.

Excess molar enthalpies have been measured with a quasi-isothermal flow calorimeter previously described [1]. Two precision positive displacement pumps deliver the liquids at programmable constant flow rates into the mixing coil sitting in the flow cell, which is included in the measure unit immersed in a water bath. In case of binary systems, the two liquids are the pure components and, in case of ternary systems, one of them is a pure component and the other the corresponding binary mixture in which the excess molar enthalpy value is known. The calorimeter is thermostated at $T = 298.15 \pm 0.01$ K. To achieve this condition, a Peltier cooler and a controlled heater actuate simultaneously to maintain the flow cell temperature constant. The calibration of the measurement system is made by simulating an exothermic mixing process by a calibration resistor. The change of heating power of the control-heater before, during and after measurements is an indirect measure for the excess enthalpy H^E. The H^E is calculated from differences in the heating power control, once the calibration procedure has been performed.

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Table 1

Experimental excess molar enthalpies of binary systems DBE + 2,2,4-trimethylpentane, DBE + 1-butanol and 2,2,4-trimethylpentane + 1-butanol at T = 298.15 K.

x	H^E/J mol^{-1}	x	H^E/J mol^{-1}	x	H^E/J mol^{-1}	x	H^E/J mol^{-1}
xDBE + (1 − x)2,2,4-trimethylpentane							
0.0497	26.88	0.2995	109.48	0.5494	120.48	0.7996	73.97
0.0997	51.00	0.3500	117.17	0.5996	115.38	0.8495	57.43
0.1497	71.17	0.3997	121.05	0.6499	107.85	0.8995	39.33
0.1998	86.08	0.4494	123.47	0.6993	99.00	0.9497	19.55
0.2501	99.90	0.4994	122.95	0.7499	87.66		
xDBE + (1 − x)1-butanol[a]							
0.0501	119.4	0.3004	624.6	0.5506	879.8	0.8000	772.8
0.1002	236.0	0.3498	698.4	0.5998	892.4	0.8501	679.1
0.1497	344.5	0.4006	762.1	0.6505	890.6	0.8994	543.1
0.2003	447.6	0.4507	814.0	0.7000	872.6	0.9493	330.1
0.2503	540.2	0.4997	853.2	0.7509	833.2		
x2,2,4-trimethylpentane + (1 − x)1-butanol							
0.0502	67.15	0.3000	395.64	0.5500	605.64	0.7995	579.93
0.1001	140.02	0.3502	449.14	0.5997	623.63	0.8501	536.22
0.1504	210.84	0.4000	497.67	0.6497	630.88	0.9000	473.31
0.2002	276.46	0.4498	540.40	0.6998	624.75	0.9506	373.88
0.2504	338.99	0.5006	578.91	0.7498	608.68		

[a] Data taken from Ref. [1].

Knowing the volumetric flow rates delivered, the molar masses and the densities of the pure compounds, the mole fractions of the mixtures obtained in the mixing coil can be calculated. The maximum absolute uncertainty of mole fraction at equimolar composition is ±0.0008. Densities of pure liquids are determined by interpolating density data obtained from Riddick et al. [3] at the measured temperature of flow delivery of the displacement pumps. Estimated densities at T = 298.15 K, were 764.10, 687.80 and 805.75 kg m^{-3} for the DBE, TMP and 1-butanol, respectively. These results agree within <0.1% with values found in the literature [4–7]. Mixtures of different compositions are studied by changing the ratio of flow rates and in this way the dependence of H^E on mole fraction can be determined. The estimated relative uncertainty of the determined H^E/J mol^{-1} is $\pm 0.01 H^E$.

3. Results and discussion

The experimental excess molar enthalpies obtained in this work for the binary mixtures DBE + TMP and TMP + 1-butanol at T = 298.15 K are listed in Table 1. Experimental data for the binary mixture DBE + 1-butanol were previously reported [1].

For binary systems, there are several models and empirical equations proposed to fit the H^E measurements. The smoothing Redlich–Kister function [8], given by Eq. (1), was fitted to the results, in which the A_i coefficients are determined by the unweighted least-squares method.

$$H^E = x(1-x)\sum_{i=1}^{n} A_i (2x-1)^{i-1} \tag{1}$$

Binary systems have also been correlated using the UNIQUAC model [9], which expression for the excess molar enthalpy is given by the equation:

$$H^E = \sum_{i=1}^{n} q_i x_i \frac{\sum_{j=1}^{n} \vartheta_j \ \Delta u_{ji} \tau_{ji}}{\sum_{j=1}^{n} \vartheta_j \tau_{ij}} \tag{2}$$

where $\vartheta_i = q_i x_i / \sum_j q_j x_j$ and q_i is the molecular surface area, obtained as the sum of the contributions of the functional groups present in the compound.

The NRTL model [10] has also been used to correlate the binary systems. In the NRTL model, the expression for the excess molar enthalpy is given by the equation:

$$H^E = -RT\sum_{i=1}^{n} x_i \eta_i \tag{3}$$

where x_i is the mole fraction of the component i and η_i is given by

$$\eta_i = \frac{\sum_{k=1}^{p} x_k \tau_{ki} G_{ki} \left[\alpha\left(\tau_{ki} - \left(\sum_{n=1}^{p} x_n \tau_{ni} G_{ni} / \sum_{l=1}^{n} x_l G_{li}\right)\right) - 1\right]}{\sum_{l=1}^{p} x_l G_{li}} \tag{4}$$

$$G_{ji} = \exp(-\alpha \tau_{ij}) \tag{5}$$

The NRTL theory assumes that the excess molar enthalpy of a multicomponent mixture depends only on the binary parameters. In this work, the non-randomness parameter α is an adjustable parameter for the three-parameter NRTL model.

Results of data correlation for the binary systems are summarized in Table 2 together with root mean square deviation, *rms*, given by

$$rms = \left[\frac{\sum_{i}^{n_{dat}} (z_{\text{exp}} - z_{\text{calc}})^2}{n_{\text{dat}} - n_{\text{par}}}\right]^{1/2} \tag{6}$$

where z_{exp}, z_{calc}, n_{dat} and n_{par} are the values of the experimental and calculated property, the number of experimental data and the number of parameters of the model respectively. The degree of the polynomic expansion of Eq. (1) was optimized using the F-test [11]. A plot of the experimental and correlated data is shown in Fig. 1a–c.

The excess molar enthalpy of the system DBE + TMP at T = 298.15 K shows endothermic behaviour ($H^E > 0$) in the whole range of composition. The best fit of the experimental data at the temperature of 298.15 K is obtained with the Redlich–Kister equation with a root mean square deviation, rms ΔH^E, of 0.5 J mol^{-1} and a maximum value of the absolute deviation, max$|\Delta H^E|$, of 1.0 J mol^{-1}. Deviations obtained with the NRTL and UNIQUAC models are almost the same. The maximum value of the excess molar enthalpy is 124 J mol^{-1}, obtained at a mole fraction of DBE about 0.45. Comparison with data for the same system and temperature reported by Peng et al. [7], shows that our data agree to within 10.2% in the range of composition $0.3 \le x \le 0.7$, being the experimental data of this work higher than those of the reference [7].

The binary system DBE + 1-butanol measured at a temperature of 298.15 K is also endothermic. The maximum value of H^E is 892 J mol^{-1}, at a mole fraction of DBE about 0.60. Redlich–Kister equation gives the best fit with a root mean square deviation, rms