Excess molar volumes and excess molar enthalpies of binary mixtures for 1,2-dichloropropane + 2-alkoxyethanol acetates at 298.15 K

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Abstract

The excess molar volumes V_m^E and excess molar enthalpies H_m^E over the whole range of composition have been measured for the binary mixtures formed by 1,2-dichloropropane (1,2-DCP) with three 2-alkoxyethanol acetates at 298.15 K and atmospheric pressure using a digital vibrating-tube densimeter and an isothermal calorimeter with flow-mixing cell, respectively. The 2-alkoxyethanol acetates are ethylene glycol monomethyl ether acetate (EGMEA), ethylene glycol monoethyl ether acetate (EGEEA), and ethylene glycol monobutyl ether acetate (EGBEA). The V_m^E of the mixture has been shown positive for EGMEA, 'S-shaped' for EGEEA, being negative at low and positive at high mole fraction of 1,2-DCP, and negative for EGBEA. All the H_m^E values for the above mixtures showed an exothermic effect (negative values) which increase with increase in carbon number of the 2-alkoxyethanol acetates, showing minimum values varying from $-374\,\mathrm{J\,mol^{-1}}$ (EGMEA) to $-428\,\mathrm{J\,mol^{-1}}$ (EGBEA) around 0.54–0.56 mol fraction of 1,2-DCP. The experimental results of H_m^E and V_m^E were fitted to Redlich–Kister equation to correlate the composition dependence of both excess properties. In this work, the experimental excess enthalpy data have been also correlated using thermodynamic models (Wilson, NRTL, and UNIQUAC) and have been qualitatively discussed.
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1. Introduction

In recent years, a number of literatures of excess thermodynamic properties have been reported to provide useful information about molecular interactions and to test the thermodynamic models. According to our recent literature survey, few experimental values of excess properties for 2-alkoxyethanol acetates with halogenated hydrocarbon have been reported, except for binary mixtures of alkyl esters and α,ω-dichloroalkane [1,2].

Continuing our research program [3,4], this paper reports measurements of V_m^E and H_m^E of binary mixtures containing 1,2-dichloropropane (1,2-DCP) and three 2-alkoxyethanol acetates which are ethylene glycol monomethyl ether acetate (EGMEA), ethylene glycol monoethyl ether acetate (EGEEA), and ethylene glycol monobutyl ether acetate (EGBEA). These glycol ether esters have better solvent activity for coating resin

than ester or ketone solvents in their evaporation rate range [5].

1,2-DCP is a polar compound whose dipole moment is 1.87 debye (D) [6] at 25 °C, self-associated by dipole–dipole interaction. Breaking of this intermolecular attraction occurs upon mixing with highly polar 2-alkoxyethanol acetates which are also strongly self-associated compounds having dipole moment, 2.1 D for EGMEA, 2.2 D for EGEEA [6], not available for EGBEA. The chain length of 2-alkoxyethanol acetate must be taken into account to explain the behavior of 1,2-DCP and 2-alkoxyethanol acetate mixtures. The main characteristics of the compounds which are responsible for the deviations from ideality are polarity and self-association.

In our previous paper [4], excess properties of 1,2-dichloropropane + 2-(2-alkoxyethoxy)ethanol showed negative deviation from ideality due to the formation of weak hydrogen bonds between the hydrogen of 1,2-DCP and oxygen of 2-(2-alkoxyethoxy)ethanol at low mole fraction of 1,2-DCP, a relatively high energy then was needed to break intramolecular hydrogen bonds of 2-(2-alkoxyethoxy)ethanol at high mole fraction of 1,2-DCP.

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The Redlich–Kister [7] equation has been fitted to both excess properties. The experimental H_m^E data were also used to test the suitability of Wilson, NRTL, and UNIQUAC models [8–10].

2. Experimental

2.1. Materials

Chemicals were obtained from Fluka (1,2-dichloropropane) and Sigma–Aldrich (2-alkoxyethanol acetates). The purity was at least 99% (except for EGEEA, whose purity was 98%). All reagents were used without further purification but degassed by means of an ultrasonic bath. In order to check purities of compounds, density ρ was measured by a vibrating-tube densimeter (model DMA-58, Anton Paar, Graz, Austria) equipped with an automatic sample changer (model SP3, Anton Paar, Graz, Austria) with a resolution $\pm 1 \times 10^{-5}$ g cm^{-3} and refractive indices n_D^{25} were measured by a refractometer (model RA-520, Kyoto Electronics, Japan) with an accuracy of ± 0.00001. Densities, refractive indices, and stated purities of the pure components are listed in Table 1 [6,11].

2.2. Apparatus and procedure

2.2.1. Density measurements

Densities ρ of pure components and their mixtures were determined with an Anton Paar DMA-58 densimeter with an accuracy $\pm 1 \times 10^{-5}$ g cm^{-3} operated in suction mode and equipped with automatic sample changer (model SP3). Mixtures were prepared by mass with a digital electronic balance (model AT-201, $\pm 1.0 \times 10^{-5}$ g, Mettler Toledo AG, Switzerland). The uncertainty of mole fraction of the mixture was estimated to be less than $\pm 1 \times 10^{-4}$. The densities, ρ of mixtures were used to calculate the excess molar volumes V_m^E according to:

$$V_m^E \,(\mathrm{cm^3\,mol^{-1}}) = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \quad (1)$$

where x_i, M_i and ρ_i, ρ are the mole fraction, molar mass, and density of component i, and density of mixtures, respectively. The estimated accuracy for the measurement of excess molar volume is $\pm 5 \times 10^{-4}$ cm^3 mol^{-1}.

2.2.2. Calorimetric measurement

Excess molar enthalpies were determined with an isothermal, heat-conduction, flow calorimeter (Calorimetry Sciences Corporation, CSC-4400, Utah, U.S.A) with a newly designed flow-mixing assembly kit (model CSC4442, Utah, U.S.A). Pressure in the calorimeter flow cell was fixed at 101.3 kPa by a back-pressure regulator (Grove valves & regulator Co., Stafford, TX, U.S.A) [12,13]. The magnitude of the measured heat signal is an important factor that has to be taken into account when selecting the total volumetric flow rate for a set of experiments; in this particular study, the selected value was 0.5 cm^3 min^{-1} for all the measurements.

The performance of the calorimeter has been examined by means of enthalpies of mixing for the systems {cyclohexane + n-hexane} (endothermic) and {water + ethanol} (exothermic) recommended as reference mixtures in isothermal calorimeters [14,15]. The comparisons were made both with results of Tanaka et al. [16] for the system {cyclohexane + n-hexane} and Chand and Fenby [17] and Costigan et al. [18] for the system {water + ethanol}. In all cases the smoothed result was within 1.6% of the previously published values [3].

The pure chemicals were pumped into the calorimeter with two digital HPLC pumps with a precision of $\pm 0.2\%$ (Acuflow Series II, Fisher Scientific, U.S.A). Each pump was calibrated by determining the volumetric flow rates from 0.01 cm^3 min^{-1} to 0.5 cm^3 min^{-1} of bi-distilled water and empirical correction equations were fitted for each pump. The determination of the mass of pumped water was measured with a digital electronic balance (model AT-201, $\pm 1.0 \times 10^{-5}$ g, Mettler Toledo AG, Switzerland). To eliminate the uncertainties in the volumetric flow rate, liquid components were kept double glass-lined jacketed bottles controlled by circulating coolant from a Haake temperature bath (PolyScience, 9100 Series, IL, U.S.A.). The newly designed flow-mixing cell is shown in Fig. 1. The calorimeter was calibrated electrically at 298.15 K by an auto-calibration mode and the temperature of the room was kept constant at (298.15 ± 0.5) K and relative humidity was controlled below 30% by glove box, which is equipped with air pump, desiccant cartridge, and hydrometer. The estimated accuracy for the excess enthalpy measurement is ± 0.7 J mol^{-1}.

Baseline values were determined by running pump I at total flow rate while pump II was turned off, then repeating with pump I off and pump II at the total flow rate. Baseline values Φ of each composition can be calculated according to following relation:

$$\Phi = \frac{\dot{q}_1 \dot{v}_1}{\dot{v}_T} + \frac{\dot{q}_2 \dot{v}_2}{\dot{v}_T} \quad (2)$$

where $\dot{q}_i$ is heat flux of component i and $\dot{v}_i$ and $\dot{v}_T$ are volumetric flow rate of components ($i = 1$, 2), and total flow rate, respectively. From volumetric flow rates, the molar masses (M_1 and M_2) and the densities (ρ_1 and ρ_2) of the pure components, the compositions (x_1 and x_2) of the mixture in the mixing cell, and the excess molar enthalpies can be determined by the relation of heat flux and the baseline value at each composition:

$$x_1 = \frac{\dot{v}_1 \rho_1 / M_1}{\{(\dot{v}_1 \rho_1 / M_1) + (\dot{v}_2 \rho_2 / M_2)\}} \quad (3)$$

Table 1
Densities ρ, refractive indices n_D, and stated purities of pure components at 298.15 K

Components	ρ (g cm^{-3})		n_D^{25}		Stated purities (%)
	Exptl.	Lit.[a]	Exptl.	Lit.[a]	
1,2-DCP	1.14895	1.14936	1.43653	1.43679	>99.0
EGMEA	0.99976	1.00033	1.39988	1.39990	>99.0
EGEEA	0.96736	0.96761	1.40311	1.40320	98.0
EGBEA	0.93512	0.94200[b]	1.41183	1.41360[b]	99.0

[a] Ref. [13], unless otherwise indicated.
[b] Ref. [6] and at 293.15 K.