

# Excess molar volumes of binary mixtures of 1,3-dimethylimidazolidin-2-one with an alkan-1-ol at the temperatures 283.15 K, 298.15 K, and 313.15 K

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Received 16 August 2006; accepted 30 September 2006

Available online 14 October 2006

## Abstract

Excess molar volumes  $V_m^E$  for (1,3-dimethylimidazolidin-2-one + an alkan-1-ol from methanol to octan-1-ol) have been determined from density measurements at  $T = (283.15, 298.15, \text{ and } 313.15)$  K over the whole composition range. The  $V_m^E$  values for the mixtures of 1,3-dimethylimidazolidin-2-one with methanol show the most negative ones at any composition and  $V_m^E$  values for (1,3-dimethylimidazolidin-2-one + an alkan-1-ol) at each temperature varies systematically from negative to positive with an increase in carbon number  $\nu$  in alkan-1-ols. The  $\nu$  dependence of  $V_m^E(x_1 = 0.5)$  values for the equimolar mixtures of (1,3-dimethylimidazolidin-2-one + an alkan-1-ol) is very similar to that of (1,1,3,3-tetramethylurea + an alkan-1-ol) at 298.15 K. From the temperature dependence of  $V_m^E(x_1 = 0.5)$  values for the equimolar mixtures of 1,3-dimethylimidazolidin-2-one with an alkan-1-ol, the coefficient  $(\partial V_m^E(x = 0.5)/\partial T)_p$  was evaluated for each mixture and its dependence of  $\nu$  was also studied.

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**Keywords:** Excess molar volumes; Binary mixture; 1,3-Dimethylimidazolidin-2-one; Alkan-1-ol

## 1. Introduction

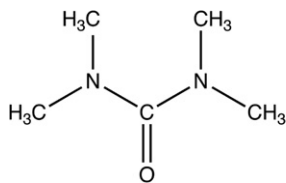
1,3-Dimethylimidazolidin-2-one (DMI) is one of the cyclic ureas and a versatile dipolar aprotic solvent [1,2]. Limited studies on physical properties of pure DMI have been carried out and only two reviews on the properties are available in the literature [3,4]. Since DMI is completely miscible with water, we have so far reported not only the excess molar volumes  $V_m^E$  from density measurements under atmospheric pressure at 298.15 K and 308.15 K [5] but also the static relative permittivities under pressures up to 300 MPa at 298.15 K [6] over the entire composition range for binary aqueous DMI mixtures. Letcher and Deenadayalu [7,8] have studied on  $V_m^E$  for binary mixtures of DMI with an alkanol or an aromatic compound at 298.15 K and atmospheric pressure. Except three papers

cited above, there is no other study on  $V_m^E$  for binary DMI mixtures; Wode and Seidel [9] have measured densities for binary aqueous DMI mixtures over the whole mole-fraction range at atmospheric pressure in the temperature range from 293.15 K to 313.15 K at intervals of 5 K only to determine the kinematic viscosities for the mixtures.

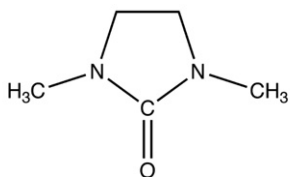
It is of much interest to study the effect of molecular shape or size on the excess thermodynamic properties such as excess molar volumes  $V_m^E$  for binary mixtures. Studies on the excess molar volumes for binary mixtures of a cyclic compound or the corresponding acyclic compound with a series of alkan-1-ols are useful to get some information on the effect of molecular shape or size on  $V_m^E$ .

In a previous paper [10], we have determined the  $V_m^E$  values for binary mixtures of 1,1,3,3-tetramethylurea (TMU) with an alkan-1-ol from methanol to butan-1-ol from density measurements using pycnometers at 298.15 K. TMU is one of the acyclic ureas and the corresponding cyclic homolog is DMI, as shown below:

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1,1,3,3-tetramethylurea



1,3-dimethylimidazolidin-2-one

A free C–N rotation in  $>C-N(CH_3)_2$  groups is feasible in a TMU molecule, but such a rotation is not allowed in a DMI molecule because of a cyclic compound. A DMI molecule has a more compact structure than a TMU molecule. A comparison of the  $V_m^E$  results for (TMU + an alkan-1-ol) with those for (DMI + an alkan-1-ol) will shed light on the effect of shape or size between the cyclic and acyclic molecules on  $V_m^E$ .

The present paper reports the new experimental  $V_m^E$  values for binary mixtures of DMI with an alkan-1-ol from methanol to octan-1-ol over the whole composition range at  $T = (283.15, 298.15, \text{ and } 313.15)$  K determined using a vibrating-tube density meter. Our  $V_m^E$  results for (DMI + an alkan-1-ol from methanol to butan-1-ol) at 298.15 K are compared with those found in the literature [7]. In addition, we make a comparison between the effect of alkyl-chain length  $\nu$  in alkan-1-ol on the equimolar excess molar volumes  $V_m^E(x_1 = 0.5)$  for (DMI + an alkan-1-ol) and that for (TMU + an alkan-1-ol), and report the temperature coefficient of  $V_m^E(x_1 = 0.5) : (\partial V_m^E(x = 0.5) / \partial T)_p$  for (DMI + an alkan-1-ol) as a function of  $\nu$  at 298.15 K.

## 2. Experimental

DMI and alkan-1-ols except heptan-1-ol were purchased from Wako Pure Chemical Industries Ltd. Heptan-1-ol was obtained from Nacalai Tesque, Inc. All of the chemicals are of guaranteed-reagent grade. Alkan-1-ols were purified by the method described in a previous paper. DMI were refluxed over  $CaH_2$  for several hours and then distilled at least twice in a stream of  $N_2$  at reduced pressure; an initial 10% distillate was discarded and then the middle fraction of distillate, corresponds to ca. 75% of the initial feed, were collected. The purity of each substance was analyzed by gas chromatography. Gas chromatographic analysis showed the major peak areas are >99.9% for DMI, methanol, ethanol, and propan-1-ol; >99.7% for butan-1-ol; >99.6% for pentan-1-ol; >99.5% for hexan-1-ol, heptan-1-ol, and octan-1-ol.

All the mixtures were prepared gravimetrically using a Mettler AE-240 balance. The uncertainty in mole fraction of DMI  $x_1$  is estimated to be less than  $3 \cdot 10^{-5}$ . Densities  $\rho$  of pure liquids and mixtures were measured with an Anton Paar DMA 58 density meter. The temperature of the density meter was controlled to 0.01 K at the desired temperature by a built-in controller and was measured with a built-in digital thermometer. The density meter was calibrated with dried air and degassed doubly distilled water

just prior to each series of density measurements. Pure liquids and each mixture were degassed ultrasonically just before density measurements by placing the tightly closed Erlenmeyer flasks in an ultrasonic bath for a few minutes. The density measurements were made at least twice for each mixture. The reproducibility in  $\rho$  is better than  $\pm 0.01 \text{ kg} \cdot \text{m}^{-3}$ . The uncertainty in each  $V_m^E$  value is estimated to be less than  $\pm 0.005 \text{ cm}^3 \cdot \text{mol}^{-1}$ .

## 3. Results and discussion

The densities  $\rho$  of pure substances determined at  $T = (283.15, 298.15, \text{ and } 313.15)$  K are listed in table 1 together with those found in the literature [2,9,11,12]. Temperature dependence of densities for each substance in the temperature range between 283.15 K and 313.15 K was correlated well with the following relation of the form:

$$\rho / (\text{kg} \cdot \text{m}^{-3}) = a + b(T/\text{K}). \quad (1)$$

Using the coefficient  $b$  and the density at 298.15 K, a cubic expansion coefficient  $\alpha_p$  at 298.15 K was evaluated for each substance. The  $\alpha_p$  values are also summarized in table 1, along with the literature values. Values of  $\rho$  at 298.15 K and 313.15 K and  $\alpha_p$  at 298.15 K for DMI agree with those found in the literature. Since the density of DMI has been so far reported at the temperatures between 293.15 K and 373.15 K, the density at 283.15 K for DMI is firstly reported; the melting temperature of DMI is around 281.3 K at atmospheric pressure. Densities at three temperatures and  $\alpha_p$  at 298.15 K for pure alkan-1-ols are in good agreement with those found in the literature.

The experimentally determined densities  $\rho$  for binary mixtures of (DMI + an alkan-1-ol) over the whole composition range at three temperatures are summarized in table 2, where the  $V_m^E$  values calculated from the following equation are also given:

$$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1}) = (x_1 M_1 + x_2 M_2) / \rho - (x_1 M_1 / \rho_1 + x_2 M_2 / \rho_2). \quad (2)$$

Here  $x_i$ ,  $\rho_i$ , and  $M_i$  are, respectively, the mole fraction, the density, and the molar mass of the component  $i$ . The  $V_m^E$  results for each mixture were fitted with the Redlich–Kister equation:

$$V_m^E / (\text{cm}^3 \cdot \text{mol}^{-1}) = x_1(1 - x_1) \sum_{i=0}^k A_i (1 - 2x_1)^i, \quad (3)$$

where  $x_1$  is the mole fraction of DMI. The parameters  $A_i$  in equation (3) determined by an unweighted least-squares method are tabulated in table 3, along with the standard deviations  $\sigma$  of the representations. The standard deviations were calculated from the equation of the form:

$$\sigma / (\text{cm}^3 \cdot \text{mol}^{-1}) = \left[ \sum_{i=0}^n (V_m^E(\text{calc.}) - V_m^E(\text{exptl.}))^2 / (n - j) \right]^{1/2}, \quad (4)$$

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