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# Determination of Excess Volumes in 1,2-Dichloroethane + Benzene, + Toluene, + p-Xylene, + Cyclohexane, and + Methylcyclohexane With a Vibrating-Tube Densimeter

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Densities of mixtures of 1,2-dichloroethane + benzene, + toluene, + p-xylene, + cyclohexane, and + methylcyclohexane were measured at 298.15 K over the whole concentration range by means of a vibrating-tube densimeter. Molar excess volumes were calculated from the results and compared to values obtained by interpolation or extrapolation of literature data.

## 1. Introduction

Mixtures of 1,2-dichloroethane (*DCE*) with hydrocarbons have been the subject of a considerable number of investigations[1–6]. This attraction is certainly due to the fact, that 1,2-dichloroethane molecules exist in two conformational isomers, the non-polar *trans* form and the polar *gauche* form, the equilibrium of which depends on the stabilization of the *gauche* form by a polarizable environment or a medium of high relative dielectric permittivity. Partly in connection with other work[7], and partly because of its intrinsic value in an intended complete thermodynamic description of selected binaries containing 1,2-dichloroethane, we have determined excess volumes $V^E$ from density measurements of the five systems *DCE* ($x_1$) + benzene ($x_2$), + toluene ($x_2$), + p-xylene ($x_2$), + cyclohexane ($x_2$), and + methylcyclohexane ($x_2$) at 298.15 K and atmospheric pressure. All measurements were

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performed with a vibrating-tube densimeter, a somewhat novel method for organic liquid mixtures, whose potential usefulness has only quite recently been realized[8]. In the following paragraph a brief description of the main features of the instrument and associated operating technique will be given. For details we refer to Ref.[9].

## 2. Experimental Part

Densities were determined with a vibrating-tube densimeter (from Sodev, Sherbrooke, Canada) operating under flow conditions. In order to maintain a constant flow rate of about 8 $mm^3 s^{-1}$, we utilized bent-axis rotary pumps[10]. The densimeter itself is based on the principle that the

Table 1. *Comparison of measured densities* $\rho$ *of the pure compounds with literature values at 298.15* K *and atmospheric pressure*

| Compound | $\rho$/g $cm^{-3}$ This work | $\rho$/g $cm^{-3}$ Lit. values |
|---|---|---|
| Benzene | 0.87370 | 0.87366[15] |
| Toluene | 0.86223 | 0.86224[15] |
| p-Xylene | 0.85694 | 0.85678[15] |
| Cyclohexane | 0.77394 | 0.77389[16] |
| Methylcyclohexane | 0.76524 | 0.76511[17] |
| 1,2-Dichloroethane | 1.24620 | 1.24563[4] |

density of a fluid contained in the U-shaped hollow oscillator of the instrument is related to the natural vibration frequency of the tube (*Kratky*, *Leopold*, and *Stabinger*[11]). Specifically, for the range of interest, the density $\rho$ is linearly related to the square of the period of vibration $\tau$, viz.

$$\rho = A + B\tau^2, \tag{1}$$

where $A$ and $B$ are constants characteristic for a particular oscillator. Upon entering the densimeter, the liquid is brought to within 0.5 mK of the desired temperature. The period of the filled tube is then measured with a high-resolution digital frequency meter (Schneider CF 700), whose output is fed directly into a printer. The instrument is set to average $10^4$ vibrational periods (ca. 30 s). The absolute temperature is determined with a calibrated Hewlett-Packard Model 2801-A quartz thermometer, and is estimated to be accurate to within $\pm$ 5 mK. Before each series of measurements, the constants $A$ and $B$ are determined by calibrating the instrument with doubly distilled and degassed water[12] [$\rho$ (298.15 K) = 0.997047 g/$cm^3$] and dry $N_2$ at atmospheric pressure [$\rho$ (298.15 K) = $1.1456 \times 10^{-3}$ g/$cm^3$].

All substances were of the best commercially available quality (Fluka, puriss.), with purities exceeding 99.5 moles per cent. They were carefully dried with molecular sieve [Union Carbide Type 4 A, $8 \times 12$ mesh (beads), from Fluka] for at least 72 hours and used without further purification. Densities of the pure compounds are listed in Table 1 along with values from the literature. Mixtures were prepared by weight in small flasks

Table 2. *Molar excess volumes $V^E$ for the five systems 1,2-dichloroethane ($x_1$) + benzene [B], + toluene [T], + p-xylene [p-X], + cyclohexane [CH], and + methylcyclohexane [MeCH] at 298.15* K

| *DCE* ($x_1$) + *B* | | *DCE* ($x_1$) + *T* | | *DCE* ($x_1$) + p-*X* | | *DCE* ($x_1$) + *CH* | | *DCE* ($x_1$) + *MeCH* | |
|---|---|---|---|---|---|---|---|---|---|
| $x_1$ | $V^E$/cm$^3$ mol$^{-1}$ | $x_1$ | $V^E$/cm$^3$ mol$^{-1}$ | $x_1$ | $V^E$/cm$^3$ mol$^{-1}$ | $x_1$ | $V^E$/cm$^3$ mol$^{-1}$ | $x_1$ | $V^E$/cm$^3$ mol$^{-1}$ |
| 0.1386 | $0.097_9$ | 0.1687 | $0.070_7$ | 0.1373 | $0.081_5$ | 0.1633 | $0.672_8$ | 0.1709 | $0.535_0$ |
| 0.2432 | $0.169_0$ | 0.3275 | $0.129_5$ | 0.2985 | $0.193_9$ | 0.2645 | $0.907_5$ | 0.2427 | $0.679_2$ |
| 0.3342 | $0.206_7$ | 0.4417 | $0.158_3$ | 0.3682 | $0.233_9$ | 0.3877 | $1.049_6$ | 0.3719 | $0.830_2$ |
| 0.4681 | $0.232_0$ | 0.5130 | $0.168_2$ | 0.4939 | $0.275_0$ | 0.4931 | $1.063_8$ | 0.4674 | $0.863_3$ |
| 0.5321 | $0.230_3$ | 0.5816 | $0.168_9$ | 0.5369 | $0.283_3$ | 0.5776 | $1.002_9$ | 0.5605 | $0.829_1$ |
| 0.6131 | $0.220_2$ | 0.6433 | $0.167_5$ | 0.6202 | $0.282_8$ | 0.6996 | $0.834_4$ | 0.6634 | $0.734_0$ |
| 0.7357 | $0.182_8$ | 0.7079 | $0.153_6$ | 0.7403 | $0.248_8$ | 0.7859 | $0.649_2$ | 0.8567 | $0.385_3$ |
| 0.8554 | $0.114_2$ | 0.7915 | $0.127_1$ | 0.8464 | $0.175_0$ | 0.8922 | $0.358_5$ | 0.8818 | $0.324_6$ |
| | | 0.9144 | $0.060_9$ | | | | | | |

(ca. 15 $cm^3$). The uncertainty in the mole fraction is believed to be not greater than 0.0001. The total uncertainty in $V^E$ introduced by drift of the instrument, uncertainty in composition etc. is estimated to be less than $\pm$ 0.004 $cm^3$/mol.

Molar quantities are based on the relative atomic mass table 1975 as issued by IUPAC[13]. Specifically, $A_r$ (H) = 1.0079, $A_r$ (C) = 12.011, and $A_r$ (Cl) = 35.453.

## 3. Results

Molar excess volumes $V^E$ were determined according to

$$V^E = x_1 M_1 (1/\rho_m - 1/\rho_1) + x_2 M_2 (1/\rho_m - 1/\rho_2). \tag{2}$$

Here, $x_1$ and $x_2$ are the mole fractions, and $V$, $\rho$, and $M$ denote the molar volume, the density, and the molar mass of the mixture (subscript $m$), and of the pure components (index 1 and 2), respectively. The results are given in Table 2. Table 3 summarizes the $n$ coefficients of the *Redlich—Kister* type polynomials obtained by least squares analysis:

Table 3. *Values of coefficients $A_i$ in Eq. (3) determined by least squares analysis, and standard deviations $\sigma$ at 298.15* K

| System | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $\sigma/cm^3\,mol^{-1}$ |
|---|---|---|---|---|---|
| *DCE* ($x_1$) + *B* ($x_2$) | 0.9341 | 0.0313 | — 0.0797 | | 0.003 |
| + *T* ($x_2$) | 0.6679 | 0.2075 | — 0.0649 | | 0.001 |
| + p-*X* ($x_2$) | 1.1138 | 0.3864 | — 0.1525 | 0.1538 | 0.002 |
| + *CH* ($x_2$) | 4.2351 | — 0.7612 | 0.2714 | — 0.1580 | 0.002 |
| + *MeCH* ($x_2$) | 3.4297 | — 0.4727 | 0.0837 | | 0.001 |

$$V^E/cm^3\,mol^{-1} = x_1 x_2 \sum_{i=0}^{n-1} A_i (x_1 - x_2)^i. \tag{3}$$

The minimum number of these needed to represent our results adequately was determined from the changes in the standard deviation $\sigma$, calculated from

$$\sigma^2 = \Sigma (V^E_{exp} - V^E_{calc})^2/(N - n), \tag{4}$$

where $N$ is the number of experimental points.

The excess volumes are positive for all systems, those of mixtures of dichloroethane with cyclohexane or methylcyclohexane being considerably larger as compared to the corresponding aromatic binaries. To the best of our knowledge (see also Ref.[14]) no experimental density data at 298.15 K have been reported on any one of these five systems, thus precluding direct comparison. However, by interpolation or extrapolation of results reported in Refs.[2–6], molar excess volumes may be estimated at this temperature for *DCE* + benzene, + toluene, + p-xylene, and + cyclohexane. Table 4 gives a comparison at equimolar concentration. With the exception of *DCE* + p-xylene from Ref.[5], and

Table 4. *Comparison of $V^E$ at 298.15* K *and equimolar concentration with extrapolated or interpolated values from literature*

| System | $V^E$/cm³ mol⁻¹ This work | Literature values |
|---|---|---|
| *DCE* + Benzene | $0.233_5$ | 0.242[2], 0.267[3], 0.246[5], 0.225[6] |
| + Toluene | $0.167_0$ | 0.190[5], 0.167[6] |
| + p-Xylene | $0.278_5$ | *0.431*[5], 0.250[6] |
| + Cyclohexane | $1.058_8$ | 1.053[4], 1.059[5], *1.507*[6] |
| + Methylcyclohexane | $0.857_4$ | |

of *DCE* + cyclohexane from Ref.[6], agreement is quite satisfactory. In both cases, substantially higher excess volumes are reported. The discrepancies amount up to about 50% of $V^E$, which magnitude is clearly far outside the combined experimental error. These two data are indicated by italics.

In conclusion, the present work illustrates again the advantages of utilising vibrating tube densimeters at flow conditions for determining the density, and hence molar excess volumes, of nonelectrolyte mixtures, that is good accuracy, easy handling, relatively short time for measurements, and rather small quantities of the constituent liquids.

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