



Activity coefficients at infinite dilution of organic solutes in N-formylmorpholine and N-methylpyrrolidone from gas–liquid chromatography

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ABSTRACT

The infinite dilution activity coefficients for 25 solutes (n-alkanes, alk-1-enes, alk-1-yne, cycloalkanes, alkylbenzenes and alcohols) were measured in N-formylmorpholine (NFM) and N-methylpyrrolidone (NMP). This was performed using the gas–liquid chromatography (glc) technique with pre-saturation of the carrier gas. The solvents that were used had significant vapour pressures at the measured temperatures and therefore pre-saturation was necessary to mitigate against solvent loss from the column. Measurements were undertaken at three temperatures, viz. $T = (333.2, 348.2, \text{ and } 363.2) \text{ K}$. The selectivities and capacities for some industrial systems of interest, typically those which are quite difficult to separate via normal distillation, were calculated from the experimental results. The activity coefficients, selectivities and capacities are discussed and compared. The work was conducted to investigate the possibility of using the studied solvents in separating alkanes (such as cyclohexane) from aromatic compounds (such as benzene) and also separating aromatic compounds (such as benzene) from alkanols (such as methanol).

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1. Introduction

Activity coefficients at infinite dilution provide a means of comparing the possibility of separating organic liquid mixtures using various solvents in extractive distillation and solvent extraction. At present, the commonly used solvents for the separation of aromatics from aliphatics using extractive distillation are N-methylpyrrolidone (NMP) and aniline, but reference has been made to other solvents [1–5]. One of these alternative solvents is N-formylmorpholine (NFM).

In order to determine whether NFM could be used in this type of separation, the infinite dilution activity coefficients for selected solute–solvent systems were used to determine the selectivity, $S_{12,s}^\infty$, which is defined as [6]:

$$S_{12,s}^\infty = \gamma_{1,s}^\infty / \gamma_{2,s}^\infty \quad (1)$$

where $\gamma_{i,s}^\infty$ is the infinite dilution activity coefficient of solute i in solvent s . This property gives an indication of the relative volatility of the two components to be separated. A larger value for selectivity will give a greater chance of an effective separation to a finite concentration. Another parameter that is useful when discussing the separation potential is the capacity, which is defined as:

$$k_{1,s}^\infty = 1 / \gamma_{1,s}^\infty \quad (2)$$

This property is a measure of the solubility of component 1 in the solvent and is indicative of the amount of solute that can be dissolved before phase separation takes place. If the value for the capacity is much less than unity then the amount of solute that can dissolve in the solvent will be low and the separation will be relatively inefficient.

In this work, the infinite dilution activity coefficients of various organic solutes (n-alkanes, alk-1-enes, alk-1-yne, cycloalkanes, alkylbenzenes and alcohols) in NMP and NFM were measured using gas–liquid chromatography (glc) (see figure 1). The experiments were conducted at temperatures of $T = (333.2, 348.2, \text{ and } 363.2) \text{ K}$.

At these temperatures, the conventional glc technique could not be used, as the high volatilities would result in the solvent being eluted from the column [7]. In order to overcome this problem, the conventional glc technique was modified by the addition of a pre-saturator; this ensured that the carrier gas was saturated with solvent prior to entering the column [8].

In this work, the selectivities and capacities of two mixtures were calculated to investigate the separation performance of the two solvents. The mixtures were cyclohexane/benzene and benzene/methanol. These mixtures were chosen because of the difficulties that are experienced during their separation, due to their exhibiting azeotropic behaviour.

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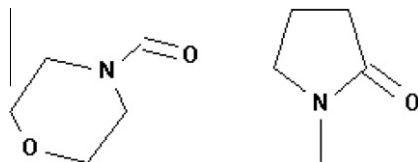


FIGURE 1. Structure of the solvents, N-formylmorpholine (left) and N-methyl-2-pyrrolidone (right).

TABLE 1
Suppliers and purity verification of solvents used in study.

Component	N-formylmorpholine	N-methylpyrrolidone
Supplier	Sigma Aldrich Co.	Merck Schuchardt OHG
GC Peak area fractions (mass fraction purity)	0.9904	0.996
Density _{meas.} /(g · cm ⁻³) (298.15 K)	1.1463	1.0296
Density _{lit.} /(g · cm ⁻³) (298.15 K)	1.14637 ^{a,b}	1.0284 ^{c,d}
R ^l _{meas.} (298.15 K)	1.4847	1.4686
R ^l _{lit.} (298.15 K)	1.485 ^b	1.4681 ^c

^a Ref. [9].

^b Ref. [10].

^c Ref. [11].

^d Ref. [12].

2. Experimental

2.1. Materials and chemicals

The suppliers of the chemicals and their purities are listed in table 1. Prior to their use, the solvents were purified by subjecting them to low pressures of approximately 5 Pa at a temperature of 313 K for 2 h. The purity of the solvents was then checked using a Shimadzu GC-2014 gas chromatograph with a Poropak packed

column of mesh size 80/100. The GC oven temperature was set to 473 K and the helium flow rate to 35 cm³ · min⁻¹. The purities (peak area fractions) of the solvents, given in table 1, were found to be better than 0.99. The densities and refractive indices of the solvents were also measured and compared against literature data [9–12] to confirm the purities (table 1). The purities of the solutes were not measured, as the GLC technique provided sufficient separation of any minor impurities present. The activity coefficient measurements were made using a Shimadzu GC-2014 gas chromatograph with Chromosorb WHP-SP 80/100 mesh solid support (supplied by Supelco), with helium (supplied by Afrox, South Africa) as the carrier gas.

2.2. Experimental procedure

The addition of a pre-saturator to the typical glc apparatus is not uncommon and has been reported previously [13–16]. In this work the pre-saturator used was similar to that used by Weidlich and co-workers [13] and Knoop and co-workers [14]. The flow-rate of the carrier gas was set by the flow controller of a Shimadzu GC-2014 gas chromatograph. A schematic diagram of the apparatus used is shown in figure 2.

The pre-saturation section of the experimental setup consisted of a 3 m length of 3.2 mm stainless steel tubing and a pre-saturator cell which was based on the dilutor cell design of Richon and Renon [17]. The cell was filled with the solvent, through which the carrier gas was bubbled from the ends of ten 50 μm internal diameter capillaries. Both the 3 m length of steel tubing and the pre-saturator were immersed in a bath of silicon oil. The temperature of the oil in the bath was kept constant by a Polyscience 8206 heating circulator and controller. The stability of the controller was stated as ±0.05 K by Polyscience. The temperature of the silicon oil near to the pre-saturator was monitored using a calibrated Pt-100 temperature probe and was set at a temperature slightly greater than that of the air bath which contained the solvent/solid support coil.

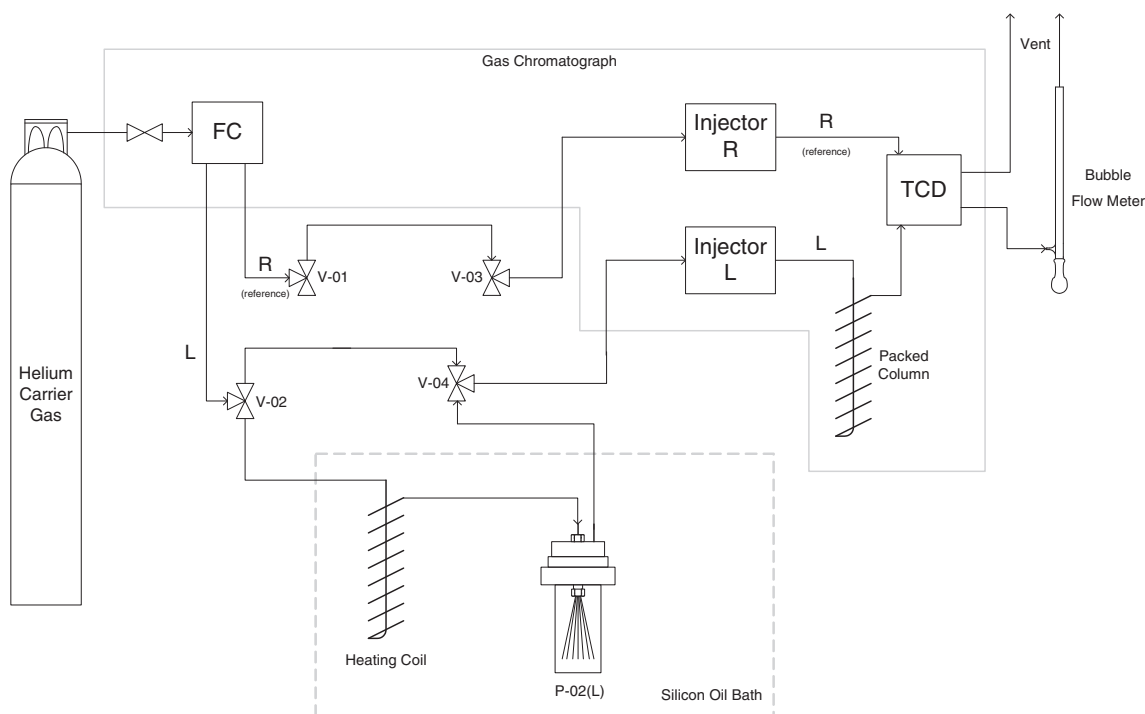


FIGURE 2. Experimental apparatus for the measurement of the infinite dilution activity coefficients of organic solutes in volatile solvents. L, sample line (left); R, reference line (right); FC, flow controller; TCD, thermal conductivity detector; V-01 – V-04, three-way valves 1 to 4; P-02(L), sample line pre-saturator.

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