ON THE DENSITY OF PURE ACETONITRILE

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Abstract

Density values for pure AN reported by several laboratories show differences well beyond experimental error, probably because of the presence of traces of water or other impurities. Density values of water – acetonitrile mixtures were measured over the whole composition range. Difficulties in obtaining absolute pureness of AN are recognized and, hence, AN with a low, but controlled, amount of water was employed. A plot including our data and those of other workers shows very good consistency and leads to an extrapolated density for pure AN of 0.77588 g.cm^{-3}, a value we recommend for precise measurements.

Resumen

Los datos obtenidos por distintos investigadores para la densidad del AN puro difieren más allá de lo que permite el error experimental, probablemente por la presencia de trazas de agua u otras impurezas. Se midieron las densidades de mezclas de agua – AN sobre todo el rango de composiciónes y, admitiendo la dificultad de asegurar el empleo de AN puro se optó por emplear AN con un contenido bajo, pero medible, de agua en la preparación de las mezclas. Se encuentra que los datos obtenidos tienen excelente acuerdo con los de la literatura y llevan, por extrapolación, a un valor de 0.77588 g.cm^{-3} para la densidad del AN puro.

Introduction

Acetonitrile (AN) is a polar solvent widely employed for industrial and research applications both as a pure solvent or in mixtures with water over the whole composition range. Thus, a significant number of research papers have been published regarding the thermodynamic properties of AN and its mixtures with water. In particular, density measurements at 298.15 K have been reported by several authors [1-9]. However, in these papers significant differences, that fall beyond experimental error, are found for the case of pure AN.

In this sense it must be emphasized that one of the major problems in obtaining reliable thermodynamic data for pure AN stems from the fact that it is very difficult to completely eliminate water from it. Consequently, even when stringent purification methods are applied, the highly hydrophilic nature of AN and the experimental limits of water detection techniques give room to the possibility that such differences might arise when highly precise experimental measurements are carried out on supposedly “water - free” AN prepared by different techniques.

In this paper we report the results obtained from precise density measurements in AN - water mixtures. Published data on the same system are compared with our results.

Experimental

Density measurements were performed employing a vibrating - tube densimeter built following the design proposed by Albert and Wood [10] as modified by Corti and Fernández Prini [11]. The experimental arrangement is schematically shown in Figure 1.

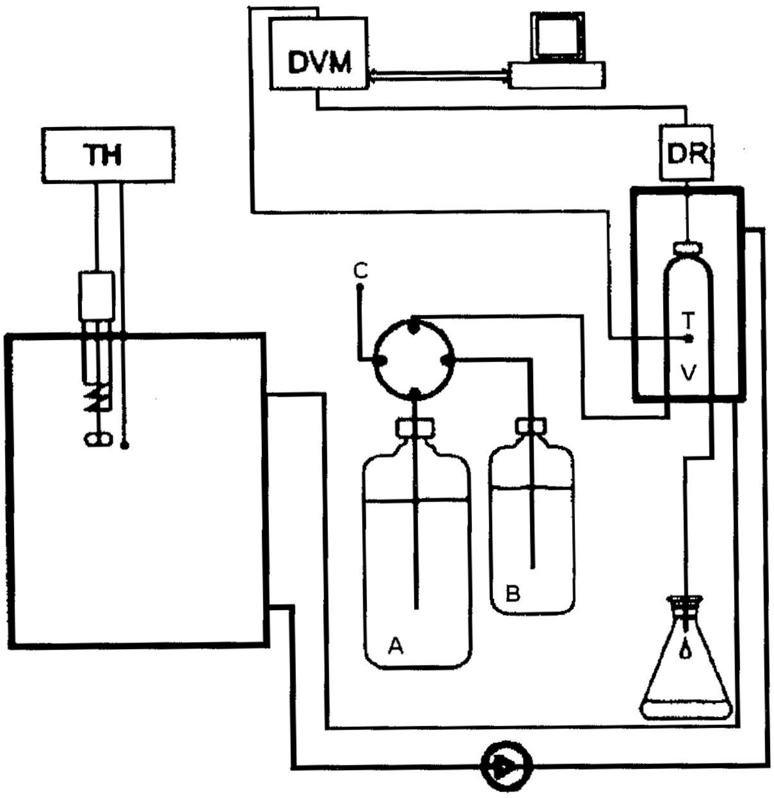

Figure 1. *Experimental set-up for the determination of density. A: water reservoir; B: sample; C: vacuum; T: thermistor; V: Vibrating tube densimeter; TH: thermostat; DVM: digital voltmeter; DR: driver.*

The densimeter employs a stainless steel U-tube, provided with a small Alnico 5 permanent magnet. The small magnet rests between two electrical coils, one designed to drive the tube and the other to pick up the tube movements. A feed back electronic unit (DR) drives the necessary current to keep the tube on resonance frequency, which is measured with a Hewlett-Packard 34401A digital multimeter. Fine-diameter (0.5 mm ID) Teflon tubing and inert fittings were employed in the flow system for fluid injection. A four-port Hamilton valve was connected to the flow system and to the vibrating tube.

For each measurement a water stationary flow was used as reference. Samples were taken from the vessel by the action of gravity and, by switching the four-port valve, alternatively water (A) and the sample (B) were introduced in the densimeter and the vibration period of the U-tube was measured. The difference between ρ_i, the density of the sample, and ρ_o, the density of water was calculated according to:

$$\Delta_i = \rho_i - \rho_o = k(\tau_i^2 - \tau_o^2) \qquad (1)$$

where τ_i and τ_o denote the vibration period of the tube when filled with the sample and water, respectively, and k is the calibration constant of the densimeter, which is determined as a function of temperature.

The densimeter unit was placed inside a much larger, thermally insulated cylindrical brass block. Heat was exchanged with a water bath. The temperature was controlled by a Lauda E200 water immersion thermostat and measured by means of a calibrated thermistor with precision better than 5 mK, using a 6 1/2 digit multimeter.

Bidistilled deionized water with specific conductance below 1 $\mu S.cm^{-1}$ was employed throughout the experiments. Pure water densities were taken from the NIST/ASME steam properties [12]. Densities were measured with precision better than $5x10^{-5}$ $g.cm^{-3}$.

Density measurements were carried out on samples prepared by weight employing spectroscopic grade AN (Aldrich >99.9% purity) with no further treatment. Chromatographic analysis of the provided AN showed no detectable impurities. Water content of this solvent was measured as in a previous work [13] water molar fraction was found to be 0.0010 ± 0.0002.

Results and discussion

Obtained density data for water-AN mixtures at 298.15 K over the whole composition range are shown in Table 1. Values published by several authors for the experimental density of “pure” AN are shown in Table 2.

Table 1: *Obtained density values for AN - water mixtures at 298.15 K*

x_{AN}	ρ/g.cm^{-3}
0.0000	0.99705
0.0510	0.97565
0.1169	0.95473
0.1971	0.92474
0.2728	0.90014
0.3601	0.87635
0.4417	0.85717
0.5204	0.84127
0.6012	0.82690
0.6671	0.81630
0.7398	0.80564
0.8253	0.79481
0.8860	0.78778
0.9389	0.78244
0.9990	0.77679

Table 2: *Pure acetonitrile*

Ref.	ρ°_{AN}/g.cm^{-3}	Remarks
1	0.7767	Density measured by pycnometry. AN fractionally distilled under nitrogen from calcium hydride.
2	0.7765	Density measured by pycnometry. AN fractionally distilled under nitrogen.
3	0.7767	Measurements were made by pycnometry, but the published values come from least squares adjustment. AN was dried over phosphorus pentoxide and fractionally distilled under nitrogen.
4	0.7778	Volumes of known masses were measured in a mercury dilatometer. AN was distilled from $KMnO_4$ and Na_2CO_3 and then fractionally distilled.
5	0.776322	Densities measured by the vibrating tube method. AN purified by storage on molecular sieves.
6	0.77649	Densities measured by the vibrating tube method. AN purified by storage on molecular sieves.
7	0.776549	Densities measured by the vibrating tube method. AN was purified by preparative gas chromatography.
8	0.77614	Densities measured by the vibrating tube method. AN purified by storage on molecular sieves.
9	0.77663	Densities measured by the vibrating tube method.

Table 3: *Experimental data obtained by different authors for AN - water mixtures with low water content*

x_{water}	ρ/g.cm^{-3}	*Reference*
0.2000	0.7977	1
0.2000	0.7975	3
0.1954	0.79659	8
0.1747	0.79481	this work
0.1500	0.7918	3
0.1168	0.7889	4
0.1140	0.78778	this work
0.1071	0.7869	9
0.1010	0.7862	1
0.1007	0.78560	8
0.1000	0.7863	3
0.0611	0.78244	this work
0.0500	0.7813	3
0.0441	0.7806	1
0.0010	0.77679	this work

As is readily seen in Table 2, discrepancies for the density of pure AN between authors are beyond what can be expected from the accuracy of the employed methods, a fact that is most probably due to differences in the impurities content of the "water free" AN employed in each case.

Thus, in order to assess the density of pure AN we have collected in Table 3 experimental points given in the literature for water - AN mixtures with water molar fractions of 0.2 or less. As shown in Figure 2 all these points nicely fit a straight line from which, by extrapolation, it is concluded that the density of pure AN is 0.77588 ± 5x10^{-5} g.cm^{-3}.

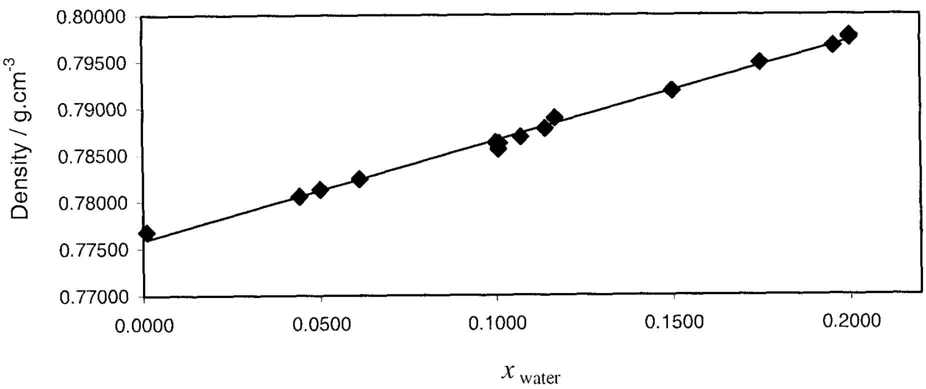

Figure 2. *Experimental density values obtained by different authors for AN - water mixtures with low water contents.*

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