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Accurate Density Determination for Solid β-1-Hexadecanol

Alan Brian Gancy

Gancy Chemical Corporation, 8810 Wandering Way, Baldwinsville, New York 13027

The density of β-1-hexadecanol has been accurately determined for the first time, employing aqueous methanol as the sink/float medium. The new density of 0.977 g cm^{-3} (15.5 °C) is compared with the only previously reported value of 0.8886 g cm^{-3} (25 °C), determined by the standard pycnometer method. The large discrepancy is attributed to an error in the pycnometer method due to inaccessibility of sample voids to the auxiliary liquid. In the sink/float approach, by contrast, the β-1-hexadecanol is in the form of microleaflets generated in situ, which form essentially a single loose somewhat spherical aggregate suspended in the sink/float medium. Evidence is presented that complications in the sink/float method as applied in the present investigation, possibly due to surface tension of the liquid medium, are eliminated by the presence of normally occurring minor impurities in high grade industrial β-1-hexadecanol.

Introduction

The production of long-chain normal aliphatic alcohols is assuming ever increasing importance in the U.S. chemical industry. Production capacity for C_6 and higher alcohols has long since exceeded 1000 tons per year (*1*). For alcohols which are solid at room temperature, the practice has been to ship and store them in the molten state. More recently, the C_{14}, C_{16}, and C_{18} alcohols are being converted to solid flake for convenience in storing, shipping, and handling. Densities of these solids are either unreported or inaccurately reported.

An extensive survey of the physical and thermodynamic properties of aliphatic alcohols (*2*) reveals that for 1-tetradecanol, densities are reported only at temperatures above the melting point, and for the supercooled liquid. For 1-octadecanol only densities above the melting point are reported. For 1-hexadecanol, liquid and supercooled liquid densities are reported, along with a single measurement on the solid well below its melting point (*3*). In the present paper it is shown that the latter value is grossly in error, being 9% lower than that determined using the sink/float method developed herein.

Sink/Float Method As Adapted to the Present Investigation

A precise method of measuring the density of minerals is described in the literature (*4*). It involves adjustment of the composition of the suspending liquid until the mineral becomes freely suspended (not floated). The density of liquid having that identical composition is then measured by a pycnometer. The mineral density is then equal to that of the liquid in which it was suspended.

In the present investigation two modifications of the above method were made.

The first modification was to generate solid β-1-hexadecanol in situ in the sink/float medium by adding water to a clear solution of the hexadecanol in methanol. The small particles generated initially digested over time at a test temperature to produce microleaflets. This was evident from the chatoyancy produced by gentle swirling of the liquid. The individual leaflets clustered into a single loose aggregate upon equilibration, undoubtedly due to van der Waals forces. It was this aggregate which functioned as the single solid entity in the sink/float determination. The purpose in employing microleaflets instead of a massive solid is to avoid the presence of voids in the solid, which would give inaccurately low density results. Preliminary experiments confirmed that undesirable voids always form upon cooling molten hexadecanol to solidification, a phenomenon for which these waxy solids are notorious. Indeed, the gross difference between the density value determined in the present work and that of the literature value is attributable to this problem of inaccessible voids in massive solid β-1-hexadecanol.

In the second modification, the density of the selfsame liquid in which study solids are suspended was measured accurately using a hydrometer. The reason is that there is a very small but nonetheless palpable solubility of the study solid, β-1-hexadecanol, in the aqueous methanol test medium used. In this case the density of β-1-hexadecanol was equal to that of the suspending medium as measured by the hydrometer. Independent density measurements were made on the known composition of aqueous methanol, at the end point, with hexadecanol absent; results were indistinguishable from those in which soluble hexadecanol was present. This result indicates that a pycnometer method could have been used in the present work. Finally, independent density measurements were made directly on the test medium, with and without suspended β-1-hexadecanol microleaflets; results were indistinguishable, indicating that the small amount of suspended solids does not interfere with the measurement of liquid density by the hydrometer. Thus, the modified method is practically, if not theoretically, sound. The solubility of β-1-hexadecanol in water at room temperature is estimated to be 1 ppm (*5*). Its solubility in the aqueous methanol suspension medium used in the present work is not precisely known, but it is less than 30 ppm at the study temperature of 15.5 °C. This is known because synthesis of an aqueous methanol solution of end point composition to contain 30 ppm hexadecanol produced copious in situ-generated solid microleaflets. In the study 30–160 ppm added hexadecanol was employed.

In practice preliminary experiments were done at the 15.5 °C test temperature to determine the approximate composition of the aqueous methanol in which the hexadecanol solids would just become suspended. The system was then "titrated" with methanol, or with water, until "just float" and "just sink" conditions were established after at least 12 h of equilibration in sealed glass vessels. Hydrometer measurements were made at both these points, and the water/methanol compositions at those points were also recorded. The final density "end point" was taken as a simple average of those hydrometer readings, and the aqueous methanol compositional end point was taken as the simple average of the two compositional

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Table I. Composition of 1-Hexadecanol Samples

	sample 1 (mass %)	sample 2 (mass %)	sample 3 (mass %)
hydrocarbon	0.9		0.45
1-dodecanol	0.79		0.40
1-tetradecanol	0.99		0.50
1-hexadecanol	97.02	99.7	98.50
1-octadecanol	0.30		0.15

Table II. Density of β-1-Hexadecanol at 15.5 °C

sample	sample purity	density (g cm^{-3})
1	97.0	0.977
2	99.7[a]	0.977
3	98.5	0.977

[a] Deliberately contaminated with 1-dodecanol; uncontaminated sample 2 gave an imprecise result.

values. The end point composition was found to be 17.65 wt % methanol/82.35 wt % water.

Near the end point the interpolation formula

$$\rho_{12} = x_1\rho_1 + x_2\rho_2$$

was found to apply, where ρ's are densities, x's are mole fractions, 1 refers to methanol, and 2 refers to water. The formula was successfully used as a guideline to determine titration increments. For example, the formula predicts that in order to increase the density of 100 g of end point liquor by 0.0005 density unit requires 2.35 g of added water. To reduce the density by 0.0005 unit requires the addition of 0.42 g of methanol.

The hydrometer used was manufactured by the Thermometer Corp. of America, Springfield, OH, and was calibrated by the manufacturer at 15.5 °C. The scale had 0.0005 specific gravity unit divisions. Specific gravity was converted to density using the known density of water at 15.5 °C.

Results

Three different β-1-hexadecanol samples were used in the study. Their compositions are given in Table I. Sample 1 was a higher purity industrial product (*6*). Sample 2 was a purified reagent grade material (*7*). Sample 3 was a 50/50 mass blend of sample 1 and sample 2; they were melted together and then solidified by cooling. Density determinations are shown in Table II.

Discussion

For sample 1 (see Table I) the end point titration was straightforward. But when a purer material, sample 2, was used, results could not be obtained within the desired limits of precision; the microleaflets tended to cling to the air/liquid interface even when they were known to be denser than the liquid. This phenomenon was undoubtedly due, at least in part, to the relatively high surface tension of the aqueous methanol suspension medium. It is reminiscent of the spreading of one liquid on another, where the condition for the spreading of substance A upon substance B is that the spreading coefficient, as defined by

$$\gamma_B - \gamma_A - \gamma_{AB}$$

be greater than zero (*8*). Here γ_B is the surface tension of substance B with respect to air (or vapor), γ_A is the surface tension of substance A with respect to air, and γ_{AB} is the tension of substance A with respect to substance B. As applied to the present situation undesirable spreading of microleaflets at the liquid/air interface is encouraged whenever the surface tension of the aqueous methanol solution with respect to air is relatively high, i.e., when γ_B is relatively high, everything else being equal.

The result using sample 1 was satisfactory; that using sample 2 was not. This suggests that the surface tension of the suspension medium used in the sample 1 determination was the lower. This, in turn, is consistent with the fact that sample 1 contains a greater amount of relatively more soluble lower fatty alcohol impurities. Such impurities would indeed act to reduce the surface tension of the suspension medium.

The Van Laar generalized multicomponent equation (*5*) predicts that, in water, the C_{14} alcohol is an order of magnitude more soluble than β-1-hexadecanol. The C_{12} alcohol is about 2 orders of magnitude more soluble. While these quantitative predictions are not necessarily confirmed, especially when methanol is present, there can be no question that lower alcohols are the more soluble. And their surface tensions are considerably lower than that of the aqueous methanol suspension medium.

An alternative explanation, of course, is that the value of γ_{AB}, the tension between the liquid and hexadecanol, is increased when the more soluble lower alcohols are present. This also tends to reduce the value of the spreading coefficient. It is conceivable that a combination of surface tension modifications is responsible for the phenomenon observed.

With the recognition that the above surface tension arguments are speculative, it was decided to test the hypothesis experimentally. Sample 2 was deliberately contaminated with single impurities known to be present in sample 1. When the contaminant was 1-octadecanol, the undesirable spreading of hexadecanol at the liquid/air interface was not eliminated. However, contamination with either 1-tetradecanol or 1-dodecanol was effective, and the formation of the familiar loose aggregate of microleaflets was observed. On the basis of these results a sink/float density determination was attempted by adding an exaggerated amount (90 ppm) of 98% pure 1-decanol to the system containing an added 90 ppm of sample 2. The attempt was successful, although the system required a longer time to reach equilibrium.

A more elegant and useful result was obtained by synthesizing a 50/50 mass blend of sample 1 and sample 2. This is designated sample 3 in Table I. The blend was produced by melting the substances together to form a homogeneous liquid and then cooling to produce a solid. This approach boosts the purity of sample 1 while at the same time retaining all of its contaminants at half-concentration. This blend, at a purity now of 98.5%, behaved satisfactorily in the density determination. Presumably the level of impurity that is effective could be further pinpointed by synthesizing blends progressively richer in sample 2.

Thus, the initial density determination using sample 1 was serendipitous because it illustrated that the sink/float method is indeed feasible. A later determination using a purer material uncovered a potential weakness of the method. However, it is seen that the weakness is easily overcome. If surface tension is indeed a factor, these findings open the door to other approaches to success, such as use of different suspension media (different, in this case, from aqueous methanol).

In any event, the density of a hypothetically pure (100%) β-1-hexadecanol can be assumed to be the same as that of the 98.5% pure sample 3 within the reported sensibility of the measurement of 0.0005 g cm^{-3}. The combined reason is that (a) the densities of the solid impurities, even if those impurities are totally associated with hexadecanol (which they are not, vide infra), are very close in magnitude to that of hexadecanol and (b) the combined concentration of impurities adds up to only 1.5% in the sample. In other words, the impurities are present in sufficient concentration to make the method feasible, but at an insufficient level to affect the ultimate density value. This conclusion is supported by the fact that measured densities in Table II are the same regardless of the impurity level.

All the known impurities are not present in a solid form so as to contaminate the solid β-1-hexadecanol. This is because the lower alcohols, known to be more soluble, are at least partially solubilized in the suspension medium. Thus, the method has a built-in self-purification feature. On the other hand, impurities known to be less soluble, such as 1-octadecanol, would tend to contaminate the leaflets relatively more than is reflected in the hexadecanol assay. The latter contamination is slight, however, considering the relatively low solubilities of both the hexadecanol and octadecanol.

The 1-hexadecanol used by previous researchers (*3*) to determine the solid density had been fractionally crystallized twice from benzene and then fractionally distilled four successive times under reduced pressure. It was presumably very pure, although an assay was not offered.

Two enantiomorphs of solid 1-hexadecanol are known, α and β, where the lower temperature form is β (*3, 9*). The reported transition temperatures vary widely, and the lowest value is 32.33 °C. Inasmuch as this is considerably higher than the 15.5 °C employed in the present work, it can be safely assumed that the form studied here is β. It would be interesting to track solid densities throughout the probable transition zone using an improved technique such as sink/float.

Conclusions

Previous researchers determined the density of solid 1-hexadecanol with a pycnometer, "water (in which the substance was found to be insoluble) being used to fill the space left unoccupied upon solidification" (*3*). In the present work this approach was found to be inadequate because not all the voids formed upon solidification were accessible to the auxiliary liquid. The pycnometer density is therefore inaccurate, being too low, for these waxy solids.

The sink/float technique employed in the present work does not suffer the consequences of inaccessible pores, and does yield the expected higher density. The resultant density is so significantly higher that it cannot be attributed to differences in impurity levels among the samples employed, but must be accounted for by some gross error such as inaccessible voids would produce.

Practical means have been employed to overcome theoretical objections to the sink/float method, e.g., the use of small amounts of suspended solids so as to allow use of a hydrometer directly on the equilibrated slurry. One potential flaw in the method, the accumulation of solids at the solution/air interface, has also been solved in a practical manner, by introducing minor amounts of impurities.

The density of β-1-hexadecanol at 15.5 °C is 0.977 g cm^{-3}, compared with the only other previously reported value of 0.8886 g cm^{-3} at 25 °C.

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