Viscosity, Freezing Point, Vapor-Liquid Equilibria, and Other Properties of Aqueous–Tetrahydrofuran Solutions

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Results are reported for the densities, viscosities, and refractive indices at 25°C for aqueous–THF solutions. The freezing points and vapor-liquid equilibrium compositions at atmospheric pressure are also reported. The results are compared with other data when available. A distillation procedure is suggested for the recovery of THF from THF solutions contaminated with small amounts of water and polymeric material. The occurrence and position of the THF–water azeotrope influence the manner of purification.

Tetrahydrofuran (THF) is a good solvent for a number of polymers and is therefore often used when measuring polymer solution properties. A large quantity of solvent is required for polymer characterization, particularly when accomplished by gel permeation chromatography. In this analysis the solvent, which is continually circulated through the apparatus, gradually becomes contaminated with small quantities of polymeric material and, particularly for THF, with water because of its hygroscopic properties. The contaminants, although present in relatively small quantities, prevent prolonged reuse of the THF solvent. The used solvent is normally disposed of and replaced by relatively costly fresh solvent.

Purification, if attempted, has usually not been successful because a single distillation cannot remove both water and polymer impurities, and the presence of an azeotrope for a composition rich in THF is not commonly known. To permit the purification of THF solvent and to extend its use as a solvent, a careful study of the properties of THF and its aqueous solutions was attempted. In addition, since references of earlier work are from journals published in five different languages, this paper may provide a useful summary of available data.

Experimental

A Fisher-certified grade of THF was purchased from Fisher Chemicals with a specified low level of impurities. The actual lot analysis for water content, THF–peroxide content, and butylated hydroxytoluene inhibitor level was specified as 0.02 wt %, 0.002%, and 0.025%, respectively. The water content of the THF as received was determined by use of standardized Karl Fisher reagent. The average of three titrations indicated 0.020 wt % water, exactly checking the specified water content. Several properties of a center fraction of THF obtained by distillation were compared with fresh undistilled THF. The comparison suggested that the THF as received indeed had a low level of impurities. Most of the solutions were prepared with THF as received with due allowance for its water content.

Distilled water was used for the preparation of the aqueous THF solutions. The solutions were prepared volumetrically by use of pipets and burets with suitable precaution for avoiding excessive exposure to moist air. The buret containing THF was equipped with a drying tube, and the aqueous solutions were prepared in 100-ml Teflon-stoppered sample bottles. The 5-ml microburet used for the dilute component had divisions of 0.01 ml so that this precision usually determined the accuracy of the solution composition.

In the preparation of solutions dilute in THF, a slight turbidity was observed at room temperature. In an attempt to define the limits of the turbid region, solutions were prepared in 1 mol % increments from 1 to 15 mol % which were slowly heated and agitated. The temperature at which the turbidity disappeared was recorded. In most cases the turbidity remained even up to the solution boiling point. The turbidity is postulated to result from the small quantity of THF inhibitor in the THF, which appears to have a limited solubility in water but is more soluble in solutions of increasing THF content. The slightly turbid solutions were cleared by filtering through a fine syringe filter of 0.45-μ porosity. On subsequent standing no further turbidity appeared. Furthermore, upon distillation of the THF, no turbidity was observed on dilution with water.

Refractive indices were measured at 25°C with a Bausch and Lomb Abbe-3L refractometer. The refractive index was subsequently used as a method of analysis for the vapor-liquid equilibrium determinations for concentrations up to 0.70 mole fraction THF.

Densities were measured at 25°C by an Anton Paar (Austria) Model DMA 02C digital precision density meter. This instrument operates on a vibrating reed principle, the frequency of which is closely related to the density of the fluid in which it is immersed. It requires calibration readings in two fluids whose densities are known, usually dried air and water. The calibrating equation for the densitometer constant (A) in terms of the vibration frequencies (T) is:

$$\rho_1 - \rho_2 = \frac{1}{A}(T_1^2 - T_2^2) \tag{1}$$

Once calibrated, the density of any other fluid could be obtained by using the known densitometer constant, the density of water, and associated with it, the vibrating frequency in water. Whereas the capability of the instrument with temperature control to ±0.001°C is to provide densities to five decimal places, the purity of the materials did not warrant this precision. Densities were reproducible to at least ±0.0001 g/ml.

Viscosities were obtained by a calibrated Cannon-Fenske viscosimeter immersed in a constant temperature, 25 ± 0.01°C, bath. The measured viscosity of 0.8940 cps for distilled water is within 0.05% of that reported in Perry (*8*) of 0.8937 cps.

Freezing points were determined in a Beckman freezing-point apparatus consisting essentially of a sample test tube equipped with stirrer and thermometer, immersed in a second insulating test tube, and the whole arrangement immersed in a cooling bath. Instead of a Beckman thermometer, an ASTM solidification-point thermometer graduated in 0.1°C was used. Methanol coolant was supplied with Dry Ice to reduce the temperature to about 10°C below the anticipated freezing point. Cooling curves were plotted, and normal freezing curves obtained

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with subcooling of no more than 0.5°C before the constant freezing point was reached. Dry Ice was not useful as a coolant for pure THF in spite of one reported freezing point of −65°C (*13*) which can be compared with the sublimation temperature for carbon dioxide of −78°C. By subsequently using liquid nitrogen as coolant, the much lower freezing point (−108.1°C) was obtained. A calibrated thermocouple was used for the THF freezing point.

The vapor-liquid equilibrium apparatus of a design suitable for measurements at atmospheric pressure is shown in Figure 1. About 100 ml of solution was charged into the apparatus which was immersed in a constant temperature bath maintained at about 5-7°C above the solution boiling point. The mercury reservoir could be lowered to vent the cell until air was excluded. The mercury reservoir was then raised to close the cell and, at the same time, to form a manometer for determining the pressure within the cell. The pressure was kept constant in a number of ways: by adjusting the bath temperature, the cooling water flow through the condenser, or by adjusting the position or exposure of the cooling tube. Hence, the measurements were made at essentially atmospheric pressure of 760 ± 2-mm mercury. A condensed vapor sample of about 8 ml was accumulated in the sample tube. A period of about 90 min was adequate for equilibrium to be established. The equilibrium compositions were measured by refractive index up to a composition of about 0.70 mole fraction THF and by standardized Karl Fischer reagent for compositions richer in THF.

Distillations for the attempted recovery of THF were performed in a 1-in. vacuum-jacketed column 48-in. in length equipped with a 2-l. still-pot, condenser, and automatically timed reflux control head. The column was packed with ¼-in. glass rings and was operated at atmospheric pressure. By use of carbon tetrachloride and toluene, the column was found equivalent to four theoretical trays for a reflux ratio of 2.9. A distillation was performed with a reflux ratio of 4:1 with a 1-l. sample of THF to which 0.50 ml of water (equivalent to 0.00305 mole fraction) had been added. The initial 15 ml of distillate contained 0.0235 mole fraction water or about eight times the water content of the original feed. Quantities of about 20 ml of distillate were successively accumulated and tested for water content with Karl Fischer reagent. The water content of the THF in the still-pot was also regularly determined. After 160 ml of distillate had been withdrawn, the water content in the still-pot was equivalent to that of fresh THF. Therefore, to achieve a better recovery of THF, an even higher reflux ratio or more effective packing was required.

The second stage of the distillation was carried out for the removal of polymeric materials. The potential recovery of usable THF from contaminated material was estimated at over 80%. The usefulness of this recovery procedure is limited by the maximum water content of the first fraction which is the azeotropic concentration. On the other hand, repeated accumulation of residues from a number of distillations in the still-pot is to be avoided because of the possible increase in concentration of the potentially explosive THF peroxide. The uninhibited product must either be re-inhibited or stored with an inert gas blanket to prevent possible peroxide formation. In our experiments, the aqueous-THF solutions were prepared immediately after distillation.

Results and Discussion

Refractive indices for aqueous-THF solutions at 25°C are listed in Table I and shown in Figure 2. Yoshioka and Taniyama (*14*) represented their refractive indices graphically, making accurate comparisons difficult. The data of Signer and coworkers (*11*) which appear in Figure 2 compare closely with that reported here. The refractive index curve can be used for accurate analysis only for solutions of concentration less than about 0.70 mole fraction THF. Above that, the change in refractive index with THF content is small.

A correction for the amount of water (0.02 wt %) present in the original THF was made to the measurements of the solution properties. At the THF-rich end of the scale, a linear extrapolation was made from essentially 99.98 wt % (99.92 mol %) to 100% for all properties measured.

The viscosities of aqueous-THF solutions at 25°C are reported in Table I and shown graphically in Figure 3. Yoshioka and Taniyama (*14*) reported solution viscosities graphically, again making actual comparisons difficult. They did, however, report a maximum viscosity of 1.743 cps at 15 mol % THF which appears to agree exactly with that reported here. The viscosity of pure THF of 0.5177 cps is appreciably higher than 0.4695 cps ob-

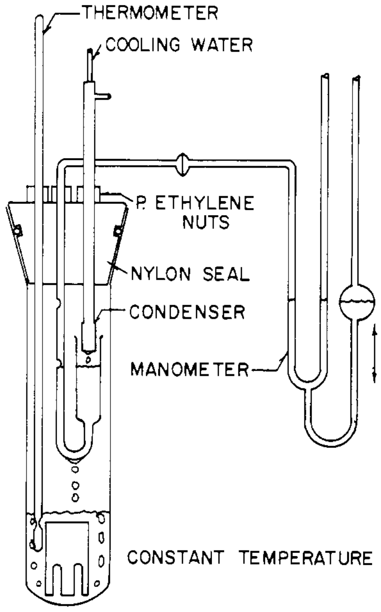

Figure 1. Vapor-liquid equilibrium apparatus

Table I. Density, Refractive Index, and Viscosity at 25°C and Freezing Points of Aqueous–THF Solutions

Mole fraction THF	Density, g/ml	Refractive index, $n^{25}D$	Viscosity, cps	Freezing point, °C
0.0	0.9971	1.3325	0.8937 (*8*)	0
0.0	0.9971	1.3325	0.8940	0
0.0423	0.9905	1.3472	1.362	3.4
0.0812	0.9838	1.3582	1.647	3.2
0.150	...	...	1.743 (*14*)	...
0.1809	0.9657	1.3758	1.741	1.2
0.3559	0.9354	1.3906	1.285	−1.0
0.5248	0.9156	1.3976	0.892	−3.7
0.7342	0.8993	1.4017	0.638	−10.0
0.8468	0.8907	1.4030	0.554	−21.0
0.9992	0.8820	1.4044	0.470	−107.5
1.00	0.88194[a]	1.4045[a]	0.4695[a]	−108.1[a]
1.00	0.8821 (*11*)	1.4048 (*11*)	0.5177 (*14*)	−108.5 (*12*)

[a] Linearly extrapolated from experimental data.

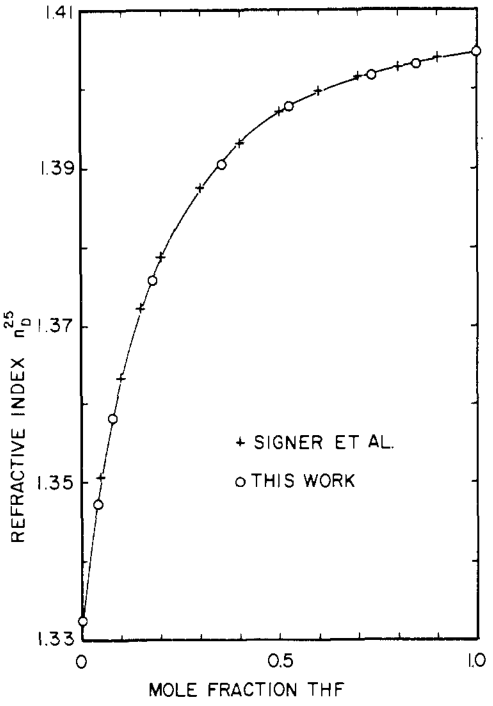

Figure 2. Refractive indices at 25°C of aqueous-THF solutions

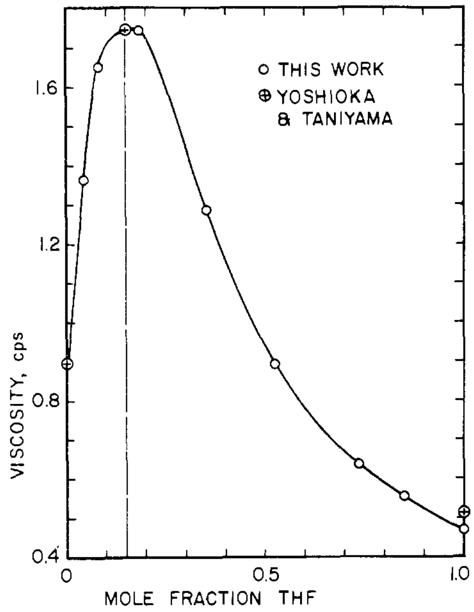

Figure 3. Viscosities at 25°C of aqueous-THF solutions

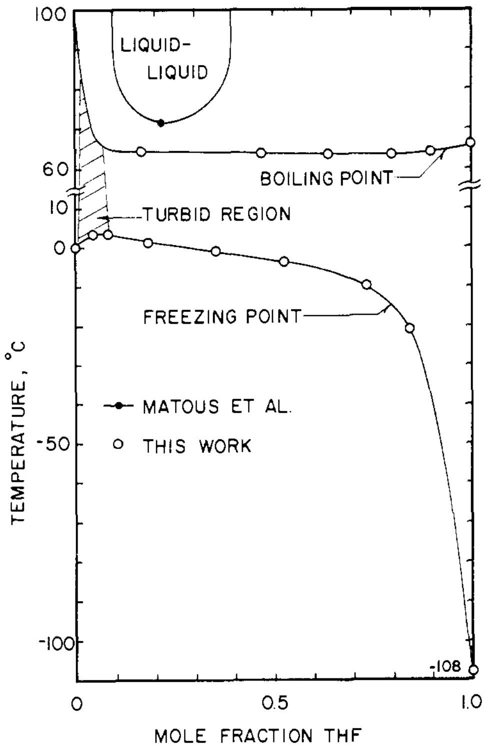

Figure 4. Phase diagram for aqueous-THF at atmospheric pressure

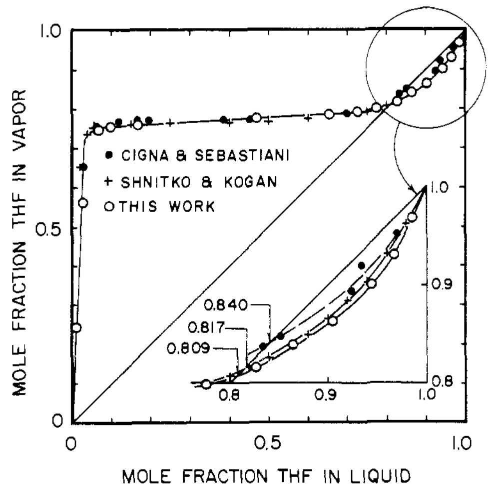

Figure 5. Vapor-liquid equilibrium for aqueous-THF at atmospheric pressure

tained in this work. Other values interpolated from the graph (*14*) were similar to those reported here except for THF-rich solutions. The solution viscosity behavior of the THF-water system appears most unusual becuase of the extremely large maximum viscosity when compared with the viscosity of either of the pure components. Qualitatively however, the viscosity behavior is similar to that for aqueous-alcohol solutions.

The densities reported in Table I conform closely to those of Signer and coworkers (*11*), with the density of pure THF reported as 0.8821 g/ml compared with 0.88194 g/ml reported here. The comparisons are similar throughout the concentration range. The molar excess volumes have been calculated by those workers. The precision for densities reported by Signer et al. was ±0.0008 g/cm^3 compared with ±0.0001 for this work. Densities of THF measured at 20° and 50°C were 0.8876 and 0.8553 g/ml, respectively.

Freezing points of aqueous-THF are also reported in Table I and graphically represented in Figure 4. The freezing point of −108.1°C for pure THF compares favorably with that reported by Sisler and coworkers (*12*) of −108.5°C. Because of the large change in freezing point with composition for THF-rich solutions, the solution freezing point appears to be a most sensitive test for water content in THF. Also shown in Figure 4 are the THF solution boiling points and a two liquid-phase region at temperatures above the solution normal boiling points

Table II. Vapor-Liquid Equilibrium Data for THF–Water at Atmospheric Pressure

Equivalent liquid compositions			Vapor composition		
Vol fraction water	Mass fraction water	Mole fraction water	Mole fraction THF, x	Mole fraction THF, y	Temp, °C
			1.00	1.00	65.7
0.0031	0.0036	0.014	0.986	0.968	...
0.0075	0.0085	0.033	0.967	0.930	...
0.0130	0.0146	0.056	0.944	0.900	...
0.0227	0.0256	0.095	0.905	0.862	64.4
0.0333	0.0375	0.135	0.865	0.839	...
0.0443	0.0500	0.174	0.826	0.816	...
0.0494	0.0555	0.191	0.809	0.809	63.8[a]
0.0602	0.0675	0.225	0.775	0.799	...
0.0763	0.0853	0.272	0.728	0.792	63.9
0.106	0.119	0.348	0.652	0.783	64.1
0.200	0.220	0.530	0.470	0.776	64.3
0.523	0.553	0.833	0.167	0.759	64.5
0.677	0.701	0.904	0.096	0.753	...
0.757	0.777	0.933	0.067	0.746	...
0.879	0.892	0.971	0.029	0.561	...
0.961	0.961	0.991	0.009	0.242	...

[a] Azeotrope.

as observed by Matous et al. (*6*) at moderate pressures. The minimum temperature at which two liquid phases could be observed was 71.8°C, corresponding to a composition of 53.5 wt %. An upper critical temperature of 137.1°C at a composition of 48 wt % was also reported. Finally, in Figure 4 is shown the concentration region in which a slight turbidity was observed on dilution of THF in (distilled) water. This turbidity, removable by filtration, was considered not to be a THF-hydrate complex or peroxide because it did not reform on standing after filtration. Instead, it appeared that this substance, which was subsequently found removable by distillation, was the inhibitor originally added to prevent peroxide formation.

Vapor-liquid equilibrium compositions at atmospheric pressure are listed in Table II and graphically shown in Figure 5. Vapor-liquid equilibrium data for this system were previously reported by Cigna and Sebastiani (*1*) and Shnitko and Kogan (*10*). An azeotrope was reported by the former workers at 84.0 mol % THF and at 81.7 mol % by the latter workers, which corresponded to a normal boiling point of 63.8° and 63.5°C, respectively. Cigna and Sebastiani also assumed the existence of a second liquid phase at the normal boiling temperature in the range from 0.08 to 0.60 mole fraction THF, chiefly on the strength of a horizontal portion of the vapor-liquid equilibrium curve. These data are shown in Figure 5 for comparison with results from this work. There is no horizontal portion to the vapor-liquid equilibrium curve; therefore, it is no surprise that a second liquid phase was not observed by Cigna and Sebastiani. The possibility of a second liquid phase at the solution boiling point has since been discounted by the work of Matous et al. (*6*) and Shnitko and Kogan (*10*). It appears possible that a slight turbidity, as observed in this work, was considered to be caused by the appearance of a second liquid phase.

The Kirk-Othmer Encyclopedia (*4*) listed THF as being completely miscible with water in all proportions. Ferguson (*2*) discussed possible reasons for the solubility of THF in water based on molecular steric effects in solution similar to that occurring with ethylene and propylene oxides. The system methyl ethyl ketone–water at 250 psia, as investigated by Othmer and coworkers (*5*, *7*), has an equilibrium relationship closely resembling that for THF–water. That system results in an increasingly flat portion of the equilibrium curve as the temperature and pressure are reduced, until finally at atmospheric pressure two immiscible liquid phases appear. For the THF–water system the work of Matous et al. (*6*) suggests completely the reverse situation in which an *increased* temperature and pressure are conducive to the formation of two immiscible phases. Further vapor-liquid equilibrium measurements both at lower and higher pressures are required to fully elucidate this interesting phase behavior.

It is perhaps indicative that Cigna and Sebastiani used the solution refractive indices as a method of analysis for the vapor and liquid compositions. That this method of analysis is somewhat insensitive to changes in water content in the THF-rich region may explain the differences in the position of the azeotrope as well as the vapor-liquid equilibrium compositions in the THF-rich region. The azeotrope, as obtained from the measurements of this work, occurs at 80.9 mol % THF, which compares favorably with that obtained by Shnitko and Kogan. These authors also found the Karl Fischer method for analysis of water content the most accurate of several methods.

Tabulations for THF properties are available in the Quaker Oats Co. bulletin (*9*) and are largely based on extrapolations and generalized calculation methods of Gallant (*3*). Some caution should be excercised in accepting these values, however, since, for example, Gallant erroneously listed the freezing point of THF as −65°C.

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