Solubility, Density, and Refractive Index of Aqueous Solutions of Pentaerythritol

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The solubility, density, and refractive index of aqueous solutions of pentaerythritol are measured over the range 30–70°C, and correlation formulas derived. The partial molar volumes and refractive indices are reported for pure hypothetical liquid pentaerythritol over this temperature range.

In consideration of the rising industrial importance of pentaerythritol (2,2-bis(hydroxymethyl)-1,3-propanediol and hereafter called Pe), the physical properties of its aqueous solutions do not appear to be well reported in the literature apart from the data of Cooke (*4*) and Kuznetsova and Gavrilova (*12*) on solubility and several spot values of density and refractive index (*10, 23*).

The Pe crystal lattice is body-centered tetragonal (*24*) at ambient temperature, and it usually crystallizes from water in the form of near-perfect tetragonal bipyramids (*17, 21*) of refractive indices 1.5559 (a) and 1.5146 (c) in sodium D light (wavelength 589 nm) (*11*), theoretical density 1.395 g/cm^3 (*13*) and melting point 265.5°C (*15*). This paper reports the solubility of Pe in water as measured by a refractometer technique and also the refractive indices and densities of solutions varying in concentration from near zero to supersaturated over the temperature range 30–70°C.

Experimental

Commercially available Pe (obtained from Hopkin and Williams Ltd.) contained as major impurities approximately 5% of an unknown formal [possibly bis-Pe-monoformal (*19, 22*) or formaldehyde bi-Pe-acetal (*1*)] and 1% diPe. The analysis was performed by the gas chromatographic separation of the trimethylsilyl ether derivatives (*20*). The Pe was purified by refluxing the aqueous solution with hydrochloric acid to hydrolyze the polyethers and extracting with active charcoal to remove hydrocarbons. The product was recrystallized from water, and analysis showed no impurities to be detectable. The purified material had a melting point of 256°C.

The solution density was determined by the principle of Archimedes (*7, 16*) by using a 50-gram glass globe of volume 33 cm^3 suspended by a fine stainless-steel wire through the base of a standard laboratory balance. Approximately 200 cm^3 of solution were used for each determination in a thermostatically jacketed beaker which was fitted with a calibrated thermometer and close-fitting insulating lid. The wire passed through a $\frac{1}{16}$-in. diam. hole in the lid; therefore, care was needed in setting up a test to insure free movement. After a change in thermostat setting, convection currents ceased within 20 min, and the balance reading became steady to within ±0.0002 gram. The apparatus was calibrated on distilled water by use of published density data (*8*). The estimated precision of the density measurement was ±0.00004 g/cm^3.

The refractive index was measured for sodium light with an Abbé refractometer (Bellingham and Stanley standard immersion type) easily capable of a precision of $\Delta n = \pm 0.0001$. The solubility was measured in a stirred thermostatic refractometer cell described elsewhere (*18*). The technique (*17*) was to add the test solution to the cell and bring it to a temperature of 80°C for several hours to condition it. It was then allowed to slowly cool at approximately 2°C/min. Readings of temperature and refractive index were taken at frequent intervals until homogeneous nucleation occurred. The temperature was then held constant at approximately the nucleation temperature until the supersaturation had been relieved, and no further change in refractive index was observed (usually overnight). This value corresponded to an equilibrium condition (which may have been pseudo) approached by growth.

The temperature was then raised several degrees and left until no further increase in refractive index was observed. This value corresponds to an equilibrium condition approached by dissolution. The temperature of the solution was raised continually in increments until all the nuclei had dissolved, and the locus of the equilibrium points intersected the original cooling curve. The test was then repeated with a solution of lower concentration, and the intersection of the cooling curve with the previous (equilibrium) heating curve gave the equilibrium concentration at that temperature (by interpolation). In this way the refractive index and solubility data were built up. No difference was detectable between the growth and dissolution equilibria. A similar technique has recently been published by Mullin (*14*).

The temperature of the cell was controlled by circulating water from a Townson and Mercer TU3 unit with a contact thermometer, and the solution temperature was indicated by calibrated mercury in a glass thermometer graduated in 0.1°C. Once a set temperature had been reached, no fluctuation in the solution temperature was detectable. The accuracy of the individual solubility points was estimated to be better than ±0.001 mass fraction.

Results

The data for solubility, density, and refractive index are presented in Tables I–III, respectively.

The solubility data were correlated by the equation:

$$\log_{10} x_1 = 0.01175t - 1.4601 \qquad (1)$$

Table I. Solubility of Pentaerythritol in Water

t, °C	x_1, mass fraction
30.0	0.0775
40.0	0.1032
50.1	0.1360
60.1	0.1772
70.2	0.2318
75.3	0.2635

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Table II. Density of Solutions of Pentaerythritol in Water (g/cm³)

x_1, mass fraction	0.025	0.050	0.070	0.090	0.110	0.130	0.150	0.170
t, °C								
21.0	1.0042	1.0104	1.0159					
25.0	1.0035	1.0098	1.0150					
28.0	1.0016	1.0086	1.0138					
30.0	1.0014	1.0075	1.0133	1.0184				
34.0	1.0004	1.0068	1.0117	1.0171	1.0223	1.0272		
38.0	0.9988	1.0051	1.0103	1.0151	1.0206	1.0257	1.0312	
40.0	0.9980	1.0041	1.0095	1.0144	1.0196	1.0247	1.0284	1.0342
44.0	0.9955	1.0022	1.0071	1.0122	1.0173	1.0225	1.0279	1.0339
48.0	0.9947	1.0008	1.0060	1.0114	1.0163	1.0211	1.0266	1.0320
50.0	0.9938	1.0002	1.0051	1.0102	1.0154	1.0186	1.0257	1.0311
54.0	0.9922	0.9983	1.0032	1.0083	1.0135	1.0175	1.0238	1.0295
58.0	0.9903	0.9961	1.0013	1.0061	1.0113	1.0164	1.0218	1.0270
60.0	0.9893	0.9954	1.0003	1.0054	1.0106	1.0157	1.0214	1.0263
64.0	0.9880	0.9940	0.9989	1.0040	1.0092	1.0142	1.0195	1.0249
68.0	0.9865	0.9910	0.9960	1.0013	1.0065	1.0112	1.0165	1.0219
70.0	0.9841	0.9899	0.9952	1.0002	1.0054	1.0104	1.0157	1.0205
74.0	0.9821	0.9882	0.9934	0.9982	1.0029	1.0078	1.0137	1.0188
78.0	0.9803	0.9860	0.9911	0.9966	1.0012	1.0053	1.0115	1.0169
80.0	0.9766	0.9854	0.9905	0.9951	1.0006	1.0045	1.0106	1.0160

Table III. Refractive Index of Solutions of Pentaerythritol in Water (Sodium D Light)

x_1, mass fraction	0.0494	0.0736	0.0974	0.1209	0.1447	0.1670	0.1896	0.2118	0.2338	0.2555
t, °C										
25.0	1.3390	1.3423	1.3458	1.3489	1.3523	1.3556	1.3590	...	...	...
30.0	1.3383	1.3417	1.3452	1.3483	1.3516	1.3549	1.3583	...	...	...
35.0	1.3377	1.3410	1.3444	1.3476	1.3509	1.3541	1.3575	1.3606	...	...
40.0	1.3370	1.3403	1.3437	1.3468	1.3501	1.3533	1.3567	1.3598	1.3631	...
45.0	1.3362	1.3395	1.3428	1.3460	1.3494	1.3525	1.3558	1.3589	1.3615	...
50.0	1.3353	1.3386	1.3420	1.3452	1.3473	1.3516	1.3549	1.3580	1.3614	1.3645
55.0	...	1.3377	1.3411	1.3434	1.3467	1.3506	1.3539	1.3570	1.3603	1.3635
60.0	...	1.3368	1.3401	1.3422	1.3464	1.3496	1.3529	1.3567	1.3592	1.3625
65.0	...	1.3357	1.3390	1.3421	1.3454	1.3485	1.3519	1.3549	1.3581	1.3610
70.0	...	...	1.3379	1.3411	1.3443	1.3471	1.3503	1.3538	1.3567	1.3601
75.0	...	...	1.3368	1.3399	1.3421	1.3462	1.3496	1.3526	1.3558	1.3590
80.0	...	...	1.3356	1.3386	1.3418	1.3451	1.3483	1.3506	1.3546	1.3574

with a standard deviation of ±0.8% of the value of x_1 which is as accurate as the experimental data warrant. The more conventional correlation of log x_1 against T^{-1} had a standard deviation of 2.6% and was therefore less useful.

The density data for a given temperature could be expressed as a linear function of composition with a standard deviation of $\pm 4 \times 10^{-5}$ (g/cm³); no useful improvement was obtained by using a second order equation. Over the temperature range considered, the slopes of the correlation lines were almost the same, having a range of only $\pm 2 \times 10^{-3}$ (g/cm³ mass fraction) and were therefore assumed parallel for the purpose of correlation. This resulted in the equation:

$$\rho_{12} = 1.0024 + 0.2573x_1 - 1.30 \times 10^{-4}t - 3.17 \times 10^{-6}t^2 \quad (2)$$

with a standard deviation of $\pm 1.5 \times 10^{-5}$ (g/cm³).

For concentrations greater than $x_1 = 0.025$ (the minimum tested), the refractive index data were correlated by the equation:

$$n^{12}\mathrm{D} = 1.3349 + 1.36 \times 10^{-1}x_1 + 1.7 \times 10^{-2}x_1{}^2 - 7.2 \times 10^{5}t - 1.15 \times 10^{-6}t^2 \quad (3)$$

with a standard deviation of $\pm 2.8 \times 10^{-5}$ refractive index units. Since some curvature occurs as $x_1 \to 0$, the extrapolation of Equation 3 gives values for the refractive index of water which are too low.

Discussion

The solubility data agree well with those of Cooke (*4*), except below 40°C where Cooke gives equilibrium concentrations about 3% greater than those found in this work. The solubility data of Kuznetsova and Gavrilova (*12*) are as much as 30% too high at 90°C; this is almost certainly due to the impure Pe used, as indicated by the low melting point of their material (200°C). When the solubility data were plotted on a basis of ln (n_1) vs. (1/T), a distinct curve resulted, indicating a heat of solution of 6.1 kcal/mol at 30°C and 7.3 kcal/mol at 75°C (endothermic) for n_1 = 0.0110 and 0.0453, respectively. The value obtained by Bright and Carson (*3*) was 5.28 kcal/mol at infinite dilution and was based on direct calorimetric measurement.

It is usual to correlate properties of mixtures with the volume fraction (Z_i) of the components where $Z_i = (n_i\bar{V}_i)/\Sigma(n_i\bar{V}_i)$; hence, in the present case for refractive index:

$$n^{12}\mathrm{D} = Z_1 n^1\mathrm{D} + Z_2 n^2\mathrm{D} \quad (4)$$

Commonly, Z_i is calculated with the molar volumes of the pure components instead of the partial molar volumes

($\bar{V}_i$) which are concentration dependent; Equation 4 therefore requires the addition of empirical correction factors. A standard procedure for determining $\bar{V}_i$ is to construct the tangent to the curve of the solution molar volume (V_{12}) against the mole fraction of solute (n_1) at the required concentration. The intercept with $n_1 = 0$ then gives $\bar{V}_2$ and with $n_1 = 1$ gives $\bar{V}_1$ for this concentration. In the present case where solutions were essentially dilute ($n_1 \ngtr 0.045$), the plot was a straight line for each temperature; in other words, the partial molar volumes remained constant within experimental error, and it was only necessary to extrapolate the best straight line to obtain $\bar{V}_1$. These values of $\bar{V}_1$ could be correlated by the linear equation:

$$\bar{V}_1 = 103.198 + 0.0274t \qquad (5)$$

with a standard deviation of $\pm 3 \times 10^{-5}$ cm^3/mol.

At 25°C the apparent molal volumes (*5*) at $x_1 = 0.03$ and 0.05 are 101.61 and 101.78 cm^3/mol, respectively, which compare with the values of Kelly et al. of 101.8 and 101.7 (*10*).

By use of Equations 3–5 and published data for n^2D (*9*), the refractive index of pure hypothetical liquid Pe was calculated as:

$$n^1\text{D} = 1.5132 - 3.6 \times 10^{-5}t - 1.16 \times 10^{-6}t^2 \qquad (6)$$

with a standard deviation of $\pm 0.1 \times 10^{-5}$ refractive index units.

The low melting point of the material used in this work was apparent rather than real: in the literature a wide range of melting points is found (*2*). The difficulty is due to a morphological change to the cubic structure which occurs at 187.7°C (*15*) with an endothermic heat of transition of 10.5 kcal/mol (*15*). Thus, the latent heat of fusion is low [1.3 kcal/mol (*6*)], in spite of the modest heat of solution. The melting point is therefore sensitive to trace impurities which have escaped the purification process. Repeated determination of the melting point by use of the same sample showed no detectable change in value, indicating that thermal decomposition during the determination had been negligible. A 0.002 mass fraction of formaldehyde in the Pe would be sufficient to depress the melting point by 5°C.

Conclusions

The solubility, density, and refractive index of aqueous solutions of Pe were determined and correlated with a good degree of precision. For a given temperature its partial molar volume did not vary with concentration (within the limits of experimental accuracy). The refractive index of pure hypothetical liquid Pe was determined, thus enabling solution refractive indices to be synthesized from component data.

Acknowledgment

The authors thank John D. Jenkins and Norman Peters of this department for their advice and assistance in preparing this paper.

Nomenclature

n_D = refractive index
n = mol fraction
M = mol weight, g/mol
t = temperature, °C
T = temperature, K
V = molar volume, cm^3/mol
$\bar{V}$ = partial molar volume, cm^3/mol
x = mass fraction
Z = volume fraction
ρ = density, g/cm^3

Subscripts

1 = Pe
2 = water
12 = solution

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Received for review October 30, 1972. Accepted November 21, 1973.