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Thermal Expansion and Shear Viscosity Coefficients of Water + Ethanol + Sucrose Mixtures

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Thermal expansion coefficients of water + ethanol + sucrose mixtures have been measured in the temperature range 10–60 °C, and shear viscosity coefficients have been measured in the temperature range 25–50 °C.

At ambient temperature the system water + ethanol exhibits large deviations from thermodynamic ideality—positive excess Gibbs free energies (*1*) and negative excess enthalpies (*2*) and volumes (*3*)—and anomalies in its viscosity (*4*). The extrema in the shear viscosity and excess enthalpy occur at an ethanol mass fraction of about 0.4. On the other hand, aqueous sucrose solutions are thermodynamically ideal, and the viscosity increases in a normal manner with increasing sucrose concentration (*5*).

We have studied the ternary system water (1) + ethanol (2) + sucrose (3) at mass fractions $w_2 \lesssim 0.3$ and $w_3 \lesssim 0.2$. Some preliminary solubility measurements at 25 °C established the solid–liquid phase diagram sketched in Figure 1. We report measurements at accessible liquid compositions at essentially 1 atm pressure of (i) the thermal expansion coefficient α_p in the range 10–60 °C and (ii) the shear viscosity coefficient η in the range 25–50 °C.

Experimental Section

Materials. The ethanol used in the dilatometry measurements and some of the viscometry measurements was AnalaR grade (British Drug Houses Ltd.); in the remaining viscometry measurements an allowance was made for a trace of water in the ethanol (<0.5%). The tap water was freshly distilled, and sucrose was a commercial sample from the British Sugar Corp.

Solutions were degassed under vacuum before use. Air solubility in water + ethanol is anomalously low (*6*), and a separate program of excess volume experiments by dilution dilatometry (*7*) had to be abandoned owing to the formation of air bubbles (despite careful degassing) on mixing ethanol with an aqueous sucrose solution.

Apparatus. The dilatometers were of the design described by Orwoll and Flory (*8*). Changes in sample volume were obtained by weighing the amounts of displaced mercury. Temperatures were measured with a Hewlett-Packard quartz-crystal thermometer in a water thermostat bath ($\lesssim$318 K, ±2 mK; $\gtrsim$318 K, ±3 mK). Appropriate corrections were made for the thermal expansion of glass and mercury (*8*).

Viscosities were measured with two Ubbelohde suspended-level viscometers (*9*). The manufacturer's calibrations were checked by measurements on distilled water from 25 to 50 °C. The passage of the meniscus was detected photoelectrically, with infrared emitters and detectors connected to the viscometer by flexible light cables (*10*). The mean flow-time was an average of five determinations. A small kinetic energy correction was applied. Shear viscosities were calculated from the measured kinematic viscosities and the densities obtained in the dilatometric work.

Table I. Thermal Expansion Coefficients for Mixtures Made from 8.31% Aqueous Ethanol

	$10^3\alpha_p$/K^{-1} sucrose mass fraction			
t/°C	0	0.0491	0.0964	0.1859
9.82	0.126	0.156	0.182	0.230
13.23	0.168	0.195	0.217	0.258
16.94	0.213	0.236	0.254	0.288
19.27	0.237	0.260	0.276	0.309
21.74	0.264	0.284	0.299	0.325
24.22	0.289	0.308	0.319	0.342
26.53	0.312	0.328	0.340	0.361
29.31	0.339	0.355	0.363	0.381
32.75	0.369	0.382	0.388	0.403
36.12	0.399	0.410	0.416	0.424
38.51	0.419	0.428	0.433	0.441
40.98	0.439	0.447	0.450	0.456
44.08	0.466	0.473	0.473	0.477
46.53	0.479	0.486	0.486	0.487
48.41	0.497	0.503	0.500	0.501
50.13	0.504	0.509	0.509	0.504
52.13	0.526	0.531	0.527	0.523
54.73	0.543	0.546	0.541	0.537
57.56	0.562	0.564	0.558	0.551
60.28	0.576	0.579	0.573	0.566

Results of Measurements

Tables I and II list isobaric thermal expansion coefficients $\alpha_p = (\partial \ln V/\partial T)_p$ from 10 to 60 °C for eight mixtures. The results in Table I are for solutions made up from a water + ethanol mixture of ethanol mass fraction $w_2 = 0.0831$ by dissolving various mass fractions w_3 of sucrose (0, 0.0491, 0.0964, and 0.1859) in the mixed solvent. (The w_2 values, therefore, do not represent the mass fractions of ethanol in the final mixture.) The results in Table II are for solutions made up from water + ethanol with $w_2 = 0.1629$. The precision of the α_p values is about 0.5%. Densities at 20.0 °C are listed in Table III, and for $w_3 = 0$ they agree with Osborn (*3*) within 0.01%.

Shear viscosity coefficients η for 15 mixtures from 25 to 50 °C are recorded in Table IV. Three different mass fractions of sucrose have been studied (0.0476, 0.0909, and 0.1667). The accuracy of the η values is estimated to be about 1%. Results

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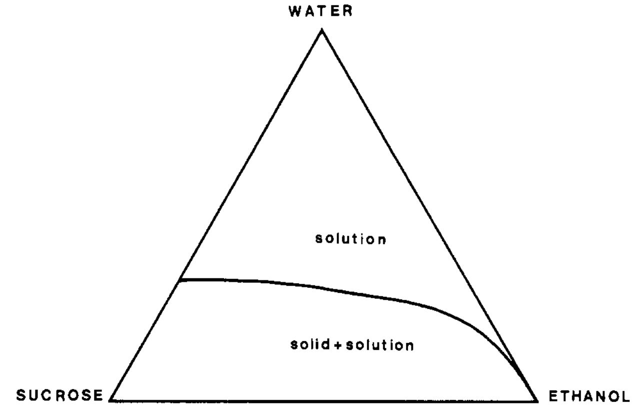

Figure 1. Solid–liquid phase diagram for water + ethanol + sucrose at 25 °C on a mass fraction basis.

Table II. Thermal Expansion Coefficients for Mixtures Made from 16.29% Aqueous Ethanol

	$10^3\alpha_p/K^{-1}$ sucrose mass fraction			
t/°C	0	0.0491	0.0964	0.1859
7.73	0.238	0.259	0.279	0.315
8.79	0.245	0.263	0.284	0.320
10.29	0.265	0.284	0.303	0.338
11.61	0.274	0.292	0.310	0.341
12.58	0.291	0.306	0.327	0.356
13.59	0.296	0.312	0.332	0.354
14.54	0.308	0.319	0.340	0.365
15.61	0.319	0.335	0.352	0.374
16.78	0.333	0.346	0.363	0.381
17.59	0.337	0.350	0.366	0.386
18.18	0.344	0.353	0.373	0.393
19.29	0.355	0.366	0.380	0.398
20.84	0.367	0.379	0.394	0.407
22.66	0.389	0.395	0.407	0.422
24.36	0.397	0.406	0.417	0.429
26.77	0.427	0.430	0.442	0.449
29.56	0.443	0.448	0.457	0.463
31.93	0.469	0.471	0.478	0.481
34.06	0.485	0.486	0.491	0.495
36.29	0.503	0.503	0.507	0.506
39.04	0.525	0.524	0.526	0.521
41.62	0.542	0.541	0.542	0.535
45.03	0.571	0.565	0.566	0.560
47.86	0.584	0.581	0.574	0.569
50.02	0.608	0.601	0.595	0.586
53.37	0.627	0.620	0.613	0.601
57.62	0.656	0.646	0.641	0.624
61.96	0.683	0.673	0.663	0.648

Table III. Densities of Water + Ethanol + Sucrose Mixtures

	ρ/g cm^{-3} sucrose mass fraction			
ethanol mass fraction	0	0.0491	0.0964	0.1859
0.0831	0.984 31	1.004 67	1.025 36	1.061 82
0.1629	0.971 75	0.993 63	1.013 67	1.053 25

for mixtures containing no ethanol agree with those of Hosking (*5*) within ±0.01 mPa s.

Discussion

The effect on α_p of adding sucrose to water + ethanol is illustrated in Figures 2 and 3 by the temperature dependence of the quantity $\Delta\alpha_p = \alpha_p - \alpha_p{}^\circ$, where the superscript ° refers to the sucrose-free mixture. At low temperatures the addition of solute increases α_p, and this is consistent with an observed depression in the temperature of maximum density in aqueous sucrose solutions (*11*). The tendency at high temperatures ($\gtrsim$40–50 °C) is for the addition of solute to reduce α_p, as one might expect with solutions of a non-hydrogen-bonding solvent.

Table IV. Shear Viscosity Coefficients for Water + Ethanol + Sucrose Mixtures

	η/mPa s					
ethanol mass fraction	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
			4.76% Sucrose			
0	1.023	0.919	0.826	0.744	0.678	0.609
0.0808	1.401	1.252	1.099	0.977	0.889	0.815
0.1648	1.822	1.593	1.376	1.218	1.090	0.982
0.2526	2.264	1.941	1.645	1.441	1.270	1.129
0.3447	2.551	2.178	1.823	1.581	1.401	1.236
			9.09% Sucrose			
0	1.159	1.036	0.934	0.848	0.772	0.706
0.0743	1.629	1.436	1.255	1.118	1.018	0.917
0.1509	2.122	1.830	1.573	1.383	1.214	1.088
0.2326	2.630	2.197	1.884	1.626	1.410	1.245
0.3172	2.978	2.475	2.108	1.805	1.571	1.380
			16.67% Sucrose			
0	1.523	1.347	1.200	1.074	0.955	0.855
0.0743	2.134	1.859	1.616	1.383	1.313	1.155
0.1509	2.766	2.373	2.036	1.781	1.581	1.396
0.2326	3.482	2.915	2.419	2.078	1.804	1.683
0.3172	4.019	3.379	2.811	2.356	2.064	1.822

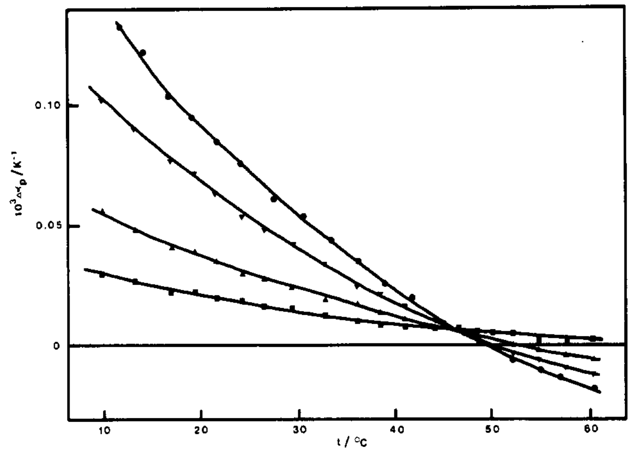

Figure 2. Effect of sucrose on the thermal expansion coefficient of a mixture of water + ethanol of ethanol mass fraction 0.0831. The change in α_p is plotted against the temperature t for various sucrose mass fractions: ■, 0.0491; ▲, 0.0964; ▼, 0.1859; ●, 0.2692.

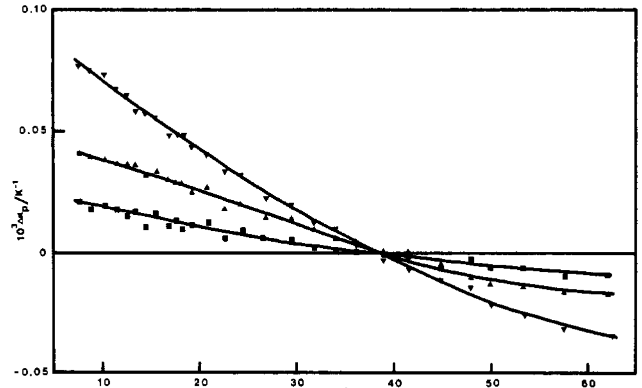

Figure 3. Effect of sucrose on the thermal expansion coefficient of a mixture of water + ethanol of ethanol mass fraction 0.1629. The change in α_p is plotted against the temperature t for various sucrose mass fractions: ■, 0.0491; ▲, 0.0964; ▼, 0.1859.

The viscosity anomaly of water + ethanol (*4*) appears to increase on adding sucrose. A 16.67% aqueous sucrose solution has a shear viscosity 1.7 times that of pure water at 25 °C, whereas if the solvent contains 30% ethanol an identical amount of sucrose increases the viscosity 2.2 times. The

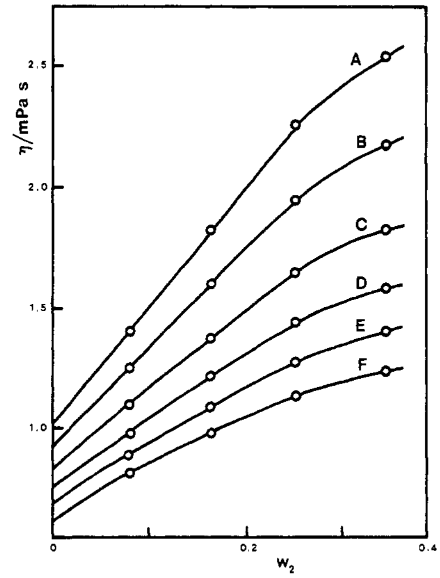

Figure 4. Shear viscosity of a 4.76% sucrose solution in water + ethanol as a function of ethanol mass fraction w_2: A, 25 °C; B, 30 °C; C, 35 °C; D, 40 °C; E, 45 °C; F, 50 °C.

anomaly reduces sharply as the temperature increases (Figure 4). Preliminary work on mixtures richer in ethanol suggests that the position of the maximum viscosity on the w_2 axis is insensitive to the amount of sucrose.

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Glossary

p	pressure
T, t	temperature
V	molar volume
w_i	mass fraction of component i
α_p	isobaric thermal expansion coefficient
η	shear viscosity coefficient
ρ	density

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Densities of Molten $FeCl_3$, $KCl-FeCl_3$, and $KCl-AlCl_3$

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Liquid densities of $FeCl_3$, $KCl-FeCl_3$, and $KCl-AlCl_3$ mixtures were measured by using the automated float method. The compositions measured for the $KCl-FeCl_3$ (and $FeCl_3$) system were in mole fractions of potassium chloride, X_{KCl}: 0.0000, 0.4000, 0.4500, 0.5000, 0.5250. The compositions measured for the $KCl-AlCl_3$ system were at X_{KCl} 0.4000 and 0.5000. The obtained densities were at each composition fitted to an equation of the form $\rho = A(X) + B(X)(t - 300)$ and $A(X)$ and $B(X)$ again fitted by polynomials of X_{KCl} in the whole mole fraction range. Furthermore, for each of the systems $KCl-FeCl_3$ and $KCl-AlCl_3$, all the measured data were fitted to an equation of form $\rho = \sum_0^n A_n X^n + (\sum_0^m B_m X^m)(t - 300)$. Interesting enough the change in molar volumes of the $KCl-FeCl_3$ mixtures was an almost linear function of the composition. Maximum deviations of only −3.5% were obtained in contrast to the deviations of up to −26% at 300 °C which can be calculated for the analogous $KCl-AlCl_3$ system. The difference between these two systems is probably due to the formation of ionic species in the molten ferric chloride in contrast to the existence of only molecular Al_2Cl_6 in liquid aluminum chloride.

In connection with a potentiometric and spectrophotometric investigation of the molten $KCl-FeCl_3$ system (*1*), the densities for this system were measured at a few compositions around a mole fraction of potassium chloride of $X_{KCl} = 0.5$ and at different temperatures. In the present paper we have supplemented these measurements to cover the mole fraction range of $0 \leq X_{KCl} \leq 0.5250$. For comparison of these densities with the densities of the $KCl-AlCl_3$ system, a few measurements have also been performed on this system. The method employed is the previously described "automated float method" for determination of densities of molten salts (*2*). This method is very well suited for the present systems, especially the $KCl-FeCl_3$ system which at compositions rich in ferric chloride has a high vapor pressure. The melt is furthermore dark colored which makes visual observations of the floats impossible. Visual observations of floats have successfully been used by other authors in connection with aluminum chloride containing systems (*3-5*), which also have high vapor pressures for mixtures rich in aluminum chloride.

Densities of the $KCl-FeCl_3$ system in a rather limited range where the vapor pressure is low and only at one temperature have been measured by the Archimedian method by Juvet, Shaw, and Khan (*6*).

Experimental Section

The densities were measured by the automated float method (*2*). This method is based on magnetic detection of quartz floats with iron cores as they pass a differential transformer. The idea is that the temperature of the melt (placed in a long tube together

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