Boiling points were correlated with the equation discussed by Wisniak and Tamir (*19*) and Tamir (*20*):

$$T = x_1T°_1 + x_2T°_2 + x_1x_2 \sum_{k=0}^{l} C_k(x_1 - x_2)^k \qquad (8)$$

An optimization technique yielded the following values of the constants:

$$C_0 = -73.8845 \qquad C_1 = 78.0144 \qquad C_2 = 63.7643 \qquad C_4 = 116.68 \qquad (9)$$

The root mean square of the fit was 0.114.

Boiling points were also correlated by a two-constant equation proposed by Wisniak (*21*):

$$T = x_1T°_1 + x_2T°_2 + Ae^{-Bx_1} \qquad (10)$$

The values of the constants were found to be $A = -457.7$ and $B = 2.725$ with a root mean square deviation of 0.399.

Acknowledgment

Yehudit Reizner and Moshe Golden helped in the experimental and numerical determinations.

Glossary

α, β, δ	constants, eq 3
A, B	constants, eq 10
B_{ii}, B_{ij}	second virial coefficient for pure component and the mixed virial coefficient, respectively
C_k	constant, eq 8
l	number of terms in the series expansion $x_1 - x_2$
P	overall pressure, mmHg
$P°_i$	vapor pressure of pure component i, mmHg
rmsd	root mean square deviation $[\sum(T_{\text{exptl}} - T_{\text{calcd}})^2/n]^{1/2}$
n	number of experimental points
t	temperature, °C
T	temperature, K
$T°_i$	boiling temperature of pure component i at pressure P, K
$V°_i$	molar volume of pure liquid component
x_i, y_i	mole fraction composition of component i in the liquid and vapor phases
γ_i	activity coefficient of component i
Λ_{ij}, Λ_{ji}	Wilson constants, eq 6 and 7

Subscript

i	component i

Registry No. 2-Propanol, 67-63-0; isopropylbenzene, 98-82-8.

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Vapor–Liquid Equilibrium in Aqueous Solutions of Various Glycols and Poly(ethylene glycols). 1. Triethylene Glycol

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The activity of water in solutions of triethylene glycol (TEG) was measured over a wide range of mole fractions at 297.6 and 332.6 K. An isopiestic method was employed, with LiCl as reference electrolyte. The calculated activity coefficients were fitted to a Van Laar equation.

Introduction

Glycols are chemicals widely used as intermediates in the preparation of various polymers or as final products (*1*). The vapor–liquid equilibrium data in aqueous solutions are important in the design of separation processes such as the removal of water from natural gas. Furthermore, they provide the basis for the understanding of such systems. The vapor–liquid equilibrium in the ethylene glycol (*2*)-, diethylene glycol (*3*)- and triethylene glycol (*4*, *5*)-water systems have been studied. A comparison of the water activity results published by Wise et al. (*4*) and Ishiguro and Matsumoto (*5*) indicates large discrepancies over a wide range of concentrations. Furthermore, in the former study (*4*) no effect of temperature was found while in the latter (*5*) the effect of temperature was significant.

The water activity in the aqueous solution of triethylene glycol was measured by an isopiestic method at 297.6 and 332.6 K. Its value is calculated from the expression

$$\ln a_w = -\nu_r m_r \phi_r / 55.51 \qquad (1)$$

where ν_r, m_r, and ϕ_r are the number of ions, the molality, and the osmotic coefficient of a reference eletrolyte. In this study LiCl was selected as reference since its osmotic coefficients can be accurately calculated over a wide range of molalities (0–18) and temperatures (273–373 K), from a correlation published by Gibbard and Scatchard (*6*).

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Table I. Isopiestic Data and Calculated Activity Coefficients

x_w[a]	m_{LiCl}[b]	ϕ[c]		a_w[d]	γ_w[e]
		LiCl	TEG		
Temperature = 297.6 K					
0.1938	18.65	3.062	0.4941	0.1280	0.6604
0.2162	17.67	3.052	0.5354	0.1435	0.6640
0.3269	14.28	2.937	0.7331	0.2210	0.6760
0.3269	14.22	2.933	0.7290	0.2228	0.6817
0.4191	12.25	2.761	0.8785	0.2960	0.7062
0.4551	11.56	2.681	0.9318	0.3277	0.7201
0.4999	10.73	2.572	0.9932	0.3703	0.7407
0.5033	10.72	2.570	1.005	0.3710	0.7371
0.6004	9.056	2.318	1.135	0.4697	0.7823
0.6102	8.887	2.290	1.147	0.4806	0.7876
0.6943	7.509	2.055	1.262	0.5738	0.8264
0.7495	6.492	1.875	1.311	0.6452	0.8608
0.7813	5.906	1.771	1.345	0.6863	0.8784
0.8106	5.284	1.662	1.352	0.7290	0.8994
0.8343	4.736	1.566	1.344	0.7657	0.9177
0.8425	4.559	1.536	1.348	0.7772	0.9225
0.8843	3.526	1.368	1.326	0.8406	0.9507
0.8923	3.365	1.341	1.346	0.8500	0.9526
0.8949	3.297	1.331	1.344	0.8539	0.9542
0.8974	3.222	1.319	1.337	0.8581	0.9563
0.9343	2.113	1.157	1.251	0.9157	0.9802
0.9359	2.061	1.150	1.245	0.9182	0.9811
0.9451	1.817	1.117	1.257	0.9295	0.9836
0.9459	1.736	1.107	1.209	0.9332	0.9866
Temperature = 332.6 K					
0.2961	15.19	2.629	0.6046	0.2375	0.8022
0.4893	10.81	2.342	0.8032	0.4019	0.8215
0.5030	10.32	2.285	0.8595	0.4278	0.8504
0.5438	9.624	2.203	0.9099	0.4661	0.8571
0.6241	8.211	2.012	0.9877	0.5517	0.8839
0.6386	7.948	1.974	0.9983	0.5684	0.8901
0.7114	6.751	1.794	1.075	0.6466	0.9088
0.7147	6.655	1.781	1.069	0.6527	0.9133
0.7571	5.896	1.665	1.101	0.7023	0.9276
0.8007	5.044	1.535	1.120	0.7567	0.9451
0.8438	4.107	1.396	1.115	0.8135	0.9641
0.8788	3.307	1.283	1.108	0.8583	0.9767
0.8830	3.229	1.273	1.117	0.8625	0.9768
0.9192	2.295	1.150	1.081	0.9094	0.9893
0.9204	2.262	1.146	1.079	0.9109	0.9897
0.9546	1.305	1.032	1.020	0.9527	0.9980

[a] Mole fraction of water. [b] Molality of LiCl. [c] Osmotic coefficient. [d] Water activity. [e] Water activity coefficient.

Experimental Section

The isopiestic apparatus consists of five silver cups, 4.0 cm in diameter and 2.5 cm high, placed in holes symmetrically drilled in a large copper plate. The copper plate was placed in a 15-cm diameter glass desiccator. Teflon covers fitted for the cups were attached to a plate held about 10 cm above the top of the cups by three rods. A slight rotation of the plate caused it to slide down on the rods and cover the cups.

Two desiccators were placed in a thermostatic bath controlled to ±0.05 K. The desiccators were rocked slowly to stir continuously the solutions.

In each run the cups with the covers were weighted accurately ($\pm 1.0 \times 10^{-5}$ g). A certain amount of LiCl (usually between 1 and 3 g) was precision weighed in three cups, while the triethylene glycol (usually 2–5 g) was weighed accurately in the other two cups. Then, distilled water was added. Its amount was calculated so that the solution compositions would bracket their expected equlibrium value. The copper plates with the cups were placed in the desiccators which were subsequently evacuated to about 20 mmHg.

Equlibrium was reached after 1–3 days, depending on the concentration of the solutions. Then the cups were covered, immediately after the desiccators were removed from the bath but prior to their opening. Each cup was weighed and the equlibrium concentrations were calculated. If the difference among the LiCl solutions or the triethylene glycol solutions in one desiccator was more than 0.3%, the point was discarded. Usually the difference was less then 0.1%.

Table II. Constants in the Van Laar Equation

temp, K	A_{12}	A_{21}	$10^3 s$[a]
297.6	−0.4849	−1.815	3.5
332.6	−0.2909	−1.000	7.7

[a] $s = [\sum_{i=1}^{n}(\gamma_{i,\mathrm{calcd}} - \gamma_{i,\mathrm{expt}})^2/(n-1)]^{1/2}$.

The purity of the triethylene glycol as stated by the manufacturer (Fluka) was better than 99%. The LiCl, manufactured by Merck Co., was analyzed by atomic absorption and titration. Its purity was greater than 99.3%. Furthermore, the LiCl dried at 120° contained less than 0.3% water, as measured by Karl Fischer analysis.

Results and Discussion

The equipment and the experimental procedure were first tested by using aqueous solutions of LiCl and NaCl. Molalities of LiCl and NaCl in equlibrium were measured at 298 K and the corresponding osmotic coefficients were calculated from the Gibbard et al. (*6*, *7*) correlation. The discrepancy between the products $m_{LiCl}\phi_{LiCl}$ and $m_{NaCl}\phi_{NaCl}$ was less than 0.5%.

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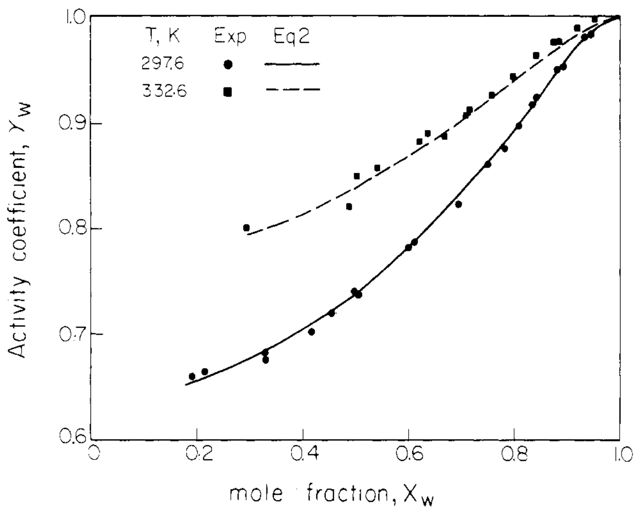

Figure 1. Activity coefficient of water as a function of its mole fraction.

Equilibrium values of the water mole fraction x_w in the triethylene glycol solution and the LiCl molalities at 297.6 and 332.6 K together with calculated values of ϕ_{LiCl} (Gibbard et al. (*6*)), a_w (eq 1), and the activity coefficient γ_w are listed in Table I. Insignificant amounts of triethylene glycol were transferred to the LiCl solutions. In Figure 1 the activity coefficients γ_w are plotted as a function of x_w. They are fitted to a Van Laar equation:

$$\ln \gamma_w = A_{12} \Big/ \left(1 + \frac{A_{12}}{A_{21}} \frac{x_w}{1 - x_w}\right)^2 \qquad (2)$$

where the constants A_{12} and A_{21} and the standard deviation of errors are given in Table II. The agreement between the predicted values from eq 2 and the experimental values is good, as shown in Figure 1.

Registry No. Water, 7732-18-5; triethylene glycol, 112-27-6.

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Ultrasonic Velocity in Polystyrene–Toluene Solutions

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Sound velocities and densities of solutions of polystyrene (PS) and styrene in toluene were measured from 10 to 50 °C at 1 atm. Three polystyrene samples having molecular weights of 9100, 290 000, and 1 840 000 were used in this study. Concentrations ranged from 0 to 20 wt % polystyrene in toluene. Sound velocity measurements accurate to better than 1 m/s were made by using a MAPCO sonic solution monitor Model 6105 while solution densities were measured by using Lipkin and bottle pycnometers. Sound velocity of the polymer solutions was found to be independent of polystyrene molecular weight over the 0–10 wt % concentration range. However, the sound velocity–concentration relation for the styrene monomer was significantly different from that of the polymer. The sound velocity–concentration relationship for polystyrene solutions at 30 °C showed slight curvature between 0 and 19.75 wt % with values of 1279.2 and 1313.1 m/s, respectively.

Introduction

There is a need for accurate thermodynamic data on dilute polymer solutions for process control applications and elucidation of solution theory. An easily measurable thermodynamic property of liquids is sound velocity. It has been demonstrated that sound velocity can be used to determine many physicochemical properties of organics (*1*,*2*). The use of sound velocity to study polymer solutions, however, has been somewhat limited.

Table I. Molecular Weights of Polymer Samples

sample	M_w	M_n	M_v	M_w/M_n
PS A		9050	9 100	<1.06
PS B	263 000	68 300	290 000	3.85
PS C	1 790 000		1 840 000	<1.30

Previous studies of polystyrene–toluene solutions by Bader and Cerf (*3*) and Dunbar et al. (*4*) have yielded conflicting results involving the sound velocity–concentration relationship. Bader (*3*) repots that sound velocity is independent of concentration from 0 to 13% whereas Dunbar (*4*) presents data showing a definite concentration dependence.

The effect of molecular weight on sound velocity in dilute polystyrene solutions was measured by Cochran et al. (*5*). He states that molecular weight has no effect on sound velocity but his values of sound velocity for 2.5% solutions of 4000 and 97 000 molecular weight polystyrene differ by as much as 4 m/s.

The purpose of this paper is to present data and to resolve the contradictions in the literature. To accomplish this objective, temperature and sound velocity were accurately measured. In addition, extreme care was taken to minimize contamination and concentration changes during measurement. The concentration dependency of the sound velocity was measured for polystyrene solutions between 0 and 19.75 wt %. The molecular weight dependency of the sound velocity was determined by using 1 and 10 wt % solutions of three different polystyrenes (9100, 290 000, and 1 840 000) in toluene.

Experimental Section

The polystyrene samples used in this study had the weight average (M_w), number average (M_n), and viscosity average (M_v) molecular weight values shown in Table I. Samples A and C