An Improved Isopiestic Method to Determine Activities in Multicomponent Mixtures

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Historically, several experimental techniques (Pytkowicz, 1979) have been employed to measure the solvent activity of multicomponent mixtures. These have included freezing point depression, boiling point elevation, dynamic and static vapor pressure measurements, osmotic pressure measurements, and the isopiestic method. Each has its positive and negative attributes. The direct measurement of the solution vapor pressure, as applied to aqueous polymer mixtures, is exemplified by the recent work of Haynes et al. (1989). However, no matter which method is used, the final objective of each of these techniques is the measurement of the solvent activity and the determination of the activity of the solute or solutes.

For nonvolatile solutes in aqueous solutions, the isopiestic method has become one of the preferred experimental techniques for the determination of solvent activities, principally because of its simplicity. A detailed example of a well-designed isopiestic apparatus and experimental procedure was described by Scatchard et al. (1938). Platford (1979) wrote a fairly complete review of the method. He pointed out the advantages of using an isotonic solution series when measuring the solvent activity of multicomponent mixtures. Adamcovà (1976) used this technique to measure the solvent activities of some aqueous salt/polymer solutions at 25°C. Herskowitz and Gottlieb (1984a,b, 1985) also used this method to determine the solvent activities of aqueous polyethylene glycol solutions. Their careful work demonstrates the kind of accuracy that can be obtained when using this method over the temperature range of 20 to 60°C. Unfortunately, the expense of this type of equipment severely handicaps many laboratories and inhibits them from studying the thermodynamics of complex solutions. Part of this problem was recently solved by Thiessen and Wilson (1987). They developed a three-legged glass apparatus that they used with a constant-temperature bath. We took their idea one step further and developed an apparatus in which the solvent activities of as many as nine solutions can be measured simultaneously.

Using the apparatus introduced here, the solvent activities of six aqueous salt/polymer systems were measured at 25°C. Two polyethylene glycols, PEG-1000 and PEG-8000, were used as the polymer components; the electrolytes $MgSO_4$, Na_2SO_4, and Na_2CO_3 were used for the salt components. Aqueous NaCl solutions were used as the primary isopiestic standards, and $MgSO_4$ solutions were used as secondary standards in those tests where the salt component was $MgSO_4$. We estimate that the average relative error in the observed water activities is ±0.02% for the data taken to date. This is sufficiently accurate to develop and refine mathematical models that describe the solution thermodynamics of aqueous polymer/polymer and aqueous salt/polymer mixtures. These mixtures are of interest because they can be made to form two-phase systems that are used for the commercial and experimental extraction and purification of biologically derived products. Examples of these systems have been described by Albertsson (1986) and by Walter et al. (1985).

Theory

The isopiestic method is the most accurate, simple experimental technique available for measuring the solvent activity of solutions that contain nonvolatile solutes. It is based on the phenomenon that different solutions, when connected through the vapor space, approach equilibrium by transferring solvent mass by distillation. The accuracy of the method depends upon the standard solutions that are used, sample mixing during the equilibration period, temperature stability, and the time allowed for the equilibration process. Equilibrium has been established once the temperature and pressure are uniform throughout the system, provided that no concentration gradients exist in the liquid phases. At equilibrium the chemical potentials of the

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solvent in each of the solutions in the closed system are identical:

$$\mu_w^\alpha = \mu_w^\beta = \cdot \cdot \cdot = \mu_w^\omega \qquad (1)$$

where μ_w is the chemical potential of the solvent in each solution α through ω. The solvent activity is related to the solvent chemical potential by

$$\ln a_w = \frac{(\mu_w - \mu_w^o)}{RT} \qquad (2)$$

where a_w is the solvent activity, R is the gas constant, μ_w^o is the standard state chemical potential of the solvent, and T is the absolute temperature. At equilibrium, equality of the solvent chemical potential implies the equality of the solvent activity. Since the solvent activity is known for one or more standard solutions, it will be known for each solution within the isopiestic system.

The standards used in aqueous solutions are usually inorganic salts for which practical osmotic coefficients have been experimentally determined to high accuracy and then correlated as functions of the salt molality. Traditionally, NaCl, KCl, $CaCl_2$, or H_2SO_4 have been used as standards. We chose the correlation of Hamer and Wu (1972) to represent the primary NaCl standards, and the correlation of Rard and Miller (1981) for the secondary $MgSO_4$ standards. The water activity can be calculated from these correlations by the use of Eq. 3:

$$\ln a_w = -0.001 \nu_s m_s M_w \phi_s \qquad (3)$$

Here, ν_s is the salt stoichiometric coefficient, m_s is the salt molality, M_w is the solvent molecular weight, and ϕ_s is the practical osmotic coefficient of the standard salt solution.

Experimental Procedure

Apparatus

The isopiestic apparatus, shown in Figure 1, consists of a multilegged manifold made of Pyrex tubing. It has nine female 20/14 standard taper ground-glass fittings attached to the legs of the manifold, and a stopcock attached to the top center of the manifold. The sample flasks were 10 mL round-bottom flasks equipped with 20/14 standard taper male ground-glass fittings.

The constant-temperature bath assembly was made by placing two tanks in series. One tank was used exclusively for temperature control while the second was used for sample equilibration. This arrangement was employed to help minimize any minor temperature variations caused by cycling in the heating/refrigeration system. The control tank was a Neslab Exacal constant-temperature bath equipped with an auxiliary refrigeration unit. The sample bath was made from an Igloo ice chest of 48 L capacity. It was equipped with a stainless steel rack to which the the isopiestic apparatus was mounted, and a flow distributor to direct the coolant down the long axis of the tank. A solution of water and antifreeze (Prestone) was used as the coolant. It was pumped through insulated Tygon tubing in a closed circuit between the two tanks and the refrigeration unit. At 25°C, the sample bath was held to within ±0.01°C over a 2h period and to within ±0.02°C over a 24 h period. The temperature of the sample bath was monitored with an ASTM mercury thermometer with a readability of ±0.01°C and a documented accuracy of ±0.01°C at 27.00°C.

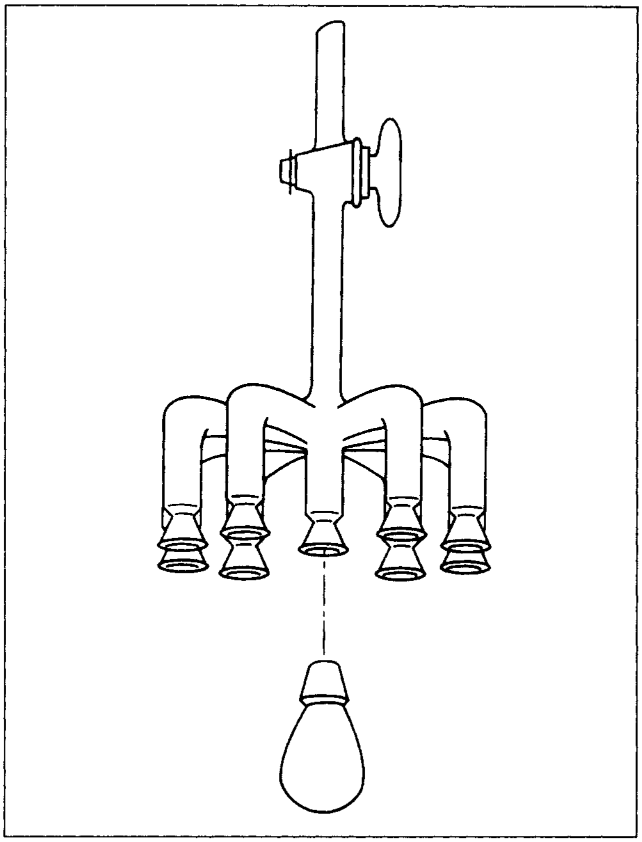

Figure 1. Isopiestic manifold.

View from below, central flask in line for mounting
Approx. dimensions: glass tubing dia., 15 mm; base dia., 20 cm; height with flasks attached, 30 cm. No dimension is critical.

Method

Reagent grade salts were used without further purification. Distilled deionized water was used as the solvent. The $MgSO_4$, Na_2SO_4, Na_2CO_3, and NaCl salts were dried in a heated vacuum desiccator at about 120°C for at least 24 h. The samples of PEG-1000 (Sigma, lot No. 19F-0337) and PEG-8000 (Sigma, lot No. 18F-0033) were used as received; they were not dried. Size exclusion chromatography was used to estimate the approximate weight average (M_{wt}) and number average (M_{no}) molecular weights of both polymers. For PEG-1000, the values found were $M_{wt} \approx 990$, and $M_{no} \approx 980$; for PEG-8000 they were $M_{wt} \approx$ 7,700, and $M_{no} \approx$ 6,400.

The nine flasks of the experimental apparatus were typically used as follows. Two flasks contained the $MgSO_4$ solutions, two flasks contained the standard NaCl solutions, one flask contained the pure polymer solution, three flasks contained the salt/polymer solutions, and the central flask was used as a water reservoir. For those tests that used Na_2SO_4 or Na_2CO_3, three flasks were filled with NaCl standards, and only one flask was filled with the second salt. The remaining flasks were utilized as outlined above, although other schemes were sometimes used.

The following procedure was used to estimate the molalities of a series of isotonic salt/polymer mixtures. First, the binodal

Table 1. Some Isopiestic Standard Solutions Used to Estimate Experimental Errors

Set No.	NaCl m	a_w*	$MgSO_4$ m	a_w**	Avg % Error
1	0.1438	0.9952	0.2415	0.9952	0.000
2	0.1519	0.9949	0.2573	0.9950	0.005
3	0.2199	0.9927	0.3724	0.9929	—
	0.2139	0.9929	—	—	—
Avg.	0.2169	0.9928	—	—	0.010
4	0.2382	0.9921	0.4142	0.9922	—
	0.2330	0.9923	—	—	—
Avg.	0.2356	0.9922	—	—	0.000
5	0.3672	0.9879	0.6621	0.9877	0.020
6	0.3926	0.9871	0.7043	0.9869	—
	0.3890	0.9872	0.6976	0.9871	—
Avg.	0.3908	0.9872	0.7010	0.9870	0.015
7	0.4181	0.9862	0.7266	0.9865	—
	0.4079	0.9866	0.7305	0.9864	—
	0.4159	0.9863	—	—	—
Avg.	0.4140	0.9864	0.7286	0.9864	0.008
8	0.6517	0.9785	1.1032	0.9789	—
	0.6358	0.9791	1.0732	0.9796	—
	0.6439	0.9786	—	—	—
Avg.	0.6438	0.9787	1.0882	0.9793	0.053
Overall % error		—	—	—	0.014

*Calculated after Hamer and Wu (1972)
**Calculated after Rard and Miller (1981)
m: molality

curve for a given system was determined and plotted so that the coordinate axes had the units of wt.% salt and wt.% polymer. Next, a reasonable value for the solvent activity was chosen. For this solvent activity, the molalities of each binary salt/H_2O and polymer/H_2O solution were calculated using an appropriate model or correlation. After conversion to the wt.% concentration scale, these points were plotted on the graph with the binodal curve and a straight line was drawn to connect them. This line approximates an isotonic series. The composition of the members of that series, each with the same solvent activity, was then chosen from that line. The line must fall below the binodal curve or else two phases will form when the solutions are mixed. The water activity that was chosen for that series must also be used to calculate the molality of the reference solutions.

The appropriate amount of each solution constituent was weighed into the solution flasks using an analytical balance accurate to ±0.1 mg. An amount of water close to the amount required to bring each sample to its estimated equilibrium concentration was weighed into each flask. The total mass of solution in each flask was designed to be about 1 g at equilibrium. To accomplish this, slightly more water than the amount required to make the solutions up to their estimated final molality was added to the central flask, typically about 0.25 g. A 3 × 10 mm Teflon-coated magnetic stir bar was placed into each flask to insure that the samples could be periodically agitated during the equilibration process.

A very light coating of silicone stopcock grease was applied to the ground-glass surfaces of each flask. They were then pressed into a fitting on the manifold and removed so that any excess grease could be wiped from the edges of the flasks and manifold. Each flask was then refitted to the manifold.

After assembly, the manifold was slowly evacuated to remove the air and to degas the solutions. It was necessary to evacuate the manifold several times because the dissolved air was slowly released from the solutions. For these experiments the degassing procedure was repeated two or three times with a 3 to 5 h waiting period between repeats. The degassing procedure removed some of the water that had been added to each flask, thus the reason for the addition of a slight excess of water to the reservoir flask. The manifold was then placed inside the sample tank and clamped to the stainless steel rack so that the stopcock was just submerged. During the equilibration process the manifold was removed at least once a day so that the samples could be agitated over a magnetic stirrer. After the third day the samples were not agitated, but left in the bath to approach their final equilibrium conditions.

In practice, the salt solutions will have approached their equilibrium concentrations in one to three days. The final equilibration between the polymer/salt mixtures and the standard salt solutions takes longer because concentration gradients tend to form in the highly viscous polymer solutions.

After equilibrium had been reached, heated air (warmer than 25°C) was admitted to the system while it was still in the bath. This prevented the condensation of water on the inner walls of the apparatus. The manifold assembly was then removed from the bath and excess coolant removed from its surface. Each flask was then removed from its arm, wiped free of grease, covered with a ground-glass stopper, cleaned of coolant, and weighed. The flasks and stoppers were then cleaned, dried, and reweighed in order to determine the final solution masses.

Results and Discussion

Table 1 contains the data that were used to estimate the error in the observed water activities. The error was calculated by

Table 2. Water Activities for Two $MgSO_4$ Systems* at 25°C

System 1			System 2		
$MgSO_4$ Wt. %	PEG-1000 Wt. %	a_w	$MgSO_4$ Wt. %	PEG-8000 Wt. %	a_w
5.19	0.0		2.40	0.0	
3.37	5.53		1.78	4.69	
2.26	9.10	0.9915	1.12	9.38	0.9959
1.44	12.21		0.58	13.77	
0.0	19.23		0.0	18.85	
7.55	0.0		5.72	0.0	
3.88	9.05		4.30	4.85	
2.09	14.69	0.9875	2.90	10.80	0.9905
0.0	24.11		1.53	17.35	
			0.0	26.01	
11.54	0.0		7.60	0.0	
8.88	4.83		5.52	6.21	
6.08	10.82	0.9793	3.58	13.02	0.9874
2.85	19.77		1.85	19.96	
0.0	30.10		0.0	28.86	
14.46	0.0		9.10	0.0	
10.82	7.92		6.60	6.56	
7.52	14.86	0.9686	4.16	14.93	0.9845
3.57	24.01		2.11	21.63	
0.0	35.82		0.0	31.13	

*System 1: PEG-1000/$MgSO_4$/H_2O
System 2: PEG-8000/$MgSO_4$/H_2O

Table 3. Water Activities for Two Na_2SO_4 Systems* at 25°C

System 1			System 2		
Na_2SO_4 Wt. %	PEG-1000 Wt. %	a_w	Na_2SO_4 Wt. %	PEG-8000 Wt. %	a_w
3.72	0.0		1.80	0.0	
2.69	4.90		1.49	4.02	
1.92	9.57	0.9893	1.06	8.75	0.9946
0.77	16.31		0.68	13.72	
0.0	22.43		0.0	21.70	
7.15	0.0		3.36	0.0	
5.32	5.51		3.04	2.05	
3.33	13.06	0.9801	2.10	9.28	0.9903
1.44	21.50		1.25	15.70	
0.0	29.98		0.0	26.67	
9.10	0.0		7.31	0.0	
6.53	6.39		6.17	3.95	
4.12	14.24	0.9748	3.91	13.11	0.9797
1.99	22.74		1.95	22.81	
0.0	32.70		0.0	34.14	
12.28	0.0		9.03	0.0	
8.15	8.77		7.18	5.78	
5.31	16.27	0.9660	4.42	15.27	0.9750
2.86	24.71		2.47	23.84	
0.0	37.11		0.0	36.60	

*System 1: PEG-1000/Na_2SO_4/H_2O
System 2: PEG-8000/Na_2SO_4/H_2O

finding the average water activity of the NaCl references, using the correlation of Hamer and Wu (1972), and comparing it to the average water activity for the $MgSO_4$ solutions, using the correlation of Rard and Miller (1981). For the entire set of experiments, the overall average error in the water activity was about ±0.02%.

Table 4. Water Activities for Two Na_2CO_3 Systems* at 25°C

System 1			System 2		
Na_2CO_3 Wt. %	PEG-1000 Wt. %	a_w	Na_2CO_3 Wt. %	PEG-8000 Wt. %	a_w
1.35	0.0		0.98	0.0	
1.04	3.43		0.78	3.45	
0.65	6.61	0.9944	0.59	7.14	0.9960
0.40	10.37		0.38	11.89	
0.0	15.47		0.0	18.93	
2.75	0.0		2.28	0.0	
2.14	3.94		1.76	5.59	
1.44	9.04	0.9892	1.19	11.55	0.9908
0.62	15.87		0.69	17.21	
0.0	22.43		0.0	26.22	
5.54	0.0		3.84	0.0	
3.72	7.13		3.09	4.45	
2.39	13.75	0.9787	2.10	12.00	0.9850
1.20	20.84		1.22	19.15	
0.0	30.00		0.0	31.03	
7.90	0.0		6.05	0.0	
4.93	9.09		4.21	8.49	
3.25	16.00	0.9699	2.93	15.13	0.9769
1.66	23.73		1.68	22.60	
0.0	35.25		0.0	35.94	

*System 1: PEG-1000/Na_2CO_3/H_2O
System 2: PEG-8000/Na_2CO_3/H_2O

Table 2 contains the concentration and water activity data for the PEG/$MgSO_4$/H_2O system. The water activities shown here are averages of the NaCl and $MgSO_4$ solutions that were used as isopiestic references. The activity and concentration data for the PEG/Na_2SO_4/H_2O system is found in Table 3. Table 4 contains the data for the PEG/Na_2CO_3/H_2O system. The water activities given in Tables 3 and 4 are the averages of the NaCl reference solutions.

There are several potential sources of random error in the experimental method described here. One major uncertainty in the absolute mass of each flask is the presence or absence of trace amounts of vacuum grease. This would be eliminated if Teflon sleeves were substituted for the silicone stopcock grease that was used. A minor source of error is the temperature stability of the sample bath.

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Notation

a = activity
M = molecular weight, $g \cdot mol^{-1}$
m = molality, $mol \cdot kg^{-1}$
R = gas constant, $J \cdot mol^{-1} \cdot K^{-1}$
T = absolute temperature, K

Greek letters

μ = chemical potential, $J \cdot mol^{-1}$
ν = stoichiometric coefficient
ϕ = practical osmotic coefficient

Subscripts

s = solute
w = solvent
wt = weight average molecular weight
no = number average molecular weight

Superscripts

$\alpha, \beta, \ldots, \omega$ = indicates phases at equilibrium
o = standard state

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