Thermodynamics of the Ternary System: Water-Glycine-Potassium Chloride at 25 °C From Vapor Pressure Measurements

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The thermodynamic properties of the ternary system: water-glycine-potassium chloride at 25 °C have been evaluated by means of isopiestic vapor pressure measurements. The effect of added glycine on the activity coefficient of potassium chloride has been calculated and the effect of added potassium chloride on the activity coefficient of glycine. The variation of the activity coefficient of potassium chloride has been studied previously by Roberts and Kirkwood, using an entirely different method—the measurement of the emf of suitable concentration cells. The agreement between these independent measurements is shown to be excellent within the concentration ranges common to both experiments.

1. Introduction

The ternary system: water-sucrose-mannitol has been investigated [1][1] by means of isopiestic vapor pressure measurements. The immediate result of such measurements is the chemical potential, or activity, of the volatile component (water) in the ternary mixture but it was shown that, provided the solvent activity could be expressed as a function of the concentrations of sucrose and mannitol, the chemical potentials of sucrose and mannitol (or their activity coefficients) could be calculated. Similar measurements have made on the systems: water-mannitol-sodium chloride [2], water-mannitol-potassium chloride [3], water-urea-sodium chloride [4], and water-sorbitol-sodium chloride [5]. It can, furthermore, be shown that once the activity coefficients of the two solutes are known as a function of concentration, then the effect of each solute on the solubility of the other can be calculated. Comparison with experimentally determined values of the solubility of each component thus provides a test both of the underlying theory and of the accuracy of the isopiestic measurements. However, by its very nature, such a test is limited to those solutions in which at least one component has the concentration of the saturated solution. It is, therefore, desirable to make a further test of the method by comparison with data for unsaturated solutions; such data are available [6] for the system: water-glycine-potassium chloride and isopiestic vapor pressure measurements are now reported for this system.

Roberts and Kirkwood [6] measured the emf of the cell: Ag, AgCl | KCl (m_c) | glycine (m_B), KCl (m_c) | AgCl, Ag and calculated therefrom the effect of glycine on the activity coefficient of potassium chloride. They expressed the activity coefficient of potassium chloride as a power series in the two concentrations:

$$2 \log \gamma_c = 2 \log \gamma_c^\circ + m_B(A + Bm_c^{1/2} + Cm_c + Dm_B) \quad (1)$$

where γ_c° is the activity coefficient of potassium chloride in a solution containing no glycine. Application of the cross-differentiation relation:

$$2\left(\frac{\partial \log \gamma_c}{\partial m_B}\right)_{m_c} = \left(\frac{\partial \log \gamma_B}{\partial m_c}\right)_{m_B} \quad (2)$$

then gives the activity coefficient of glycine as:

$$\log \gamma_B = \log \gamma_B^\circ + m_c(A + \tfrac{2}{3}Bm_c^{1/2} + \tfrac{1}{2}Cm_c + 2 Dm_B) \quad (3)$$

Thus both activity coefficients can be calculated from experiments the immediate result of which is the activity coefficient of potassium chloride. The isopiestic measurements described in this paper lead directly to a knowledge of the water activity and thence to the activity coefficients of glycine and potassium chloride. Comparison of the results, therefore, involves two different experimental techniques.

2. Method

If a solution containing glycine at a molality m_B and potassium chloride at a molality m_c is in isopiestic

[1] Figures in brackets indicate the literature references at the end of this paper.

or vapor-phase equilibrium with a (reference) solution of potassium chloride of molality m_{ref}, then the following relation must be true:

$$-55.51 \ln a_w = 2 m_{ref} \varphi_{ref} \qquad (4)$$

where a_w is the water activity of each solution and φ_{ref} is the osmotic coefficient of potassium chloride in the reference solution. Values of φ_{ref} have been tabulated [7]. A function, Δ, is defined as:

$$\Delta = -55.51 \ln a_w - m_B \varphi_B^\circ - 2 m_c \varphi_c^\circ \qquad (5)$$

where φ_B° is the osmotic coefficient of a solution containing glycine only at a molality m_B and φ_c° is the osmotic coefficient of a solution containing potassium chloride only at a molality m_c. An equation for φ_B° as a function of m_B has been given recently [8].

If Δ can be expressed as a function of m_B and m_c of the form:

$$\Delta = m_B m_c [f(m_B) + F(m_c)], \qquad (6)$$

where $f(m_B)$ is a function of m_B only and $F(m_c)$ is a function of m_c only, then it can be shown [1] that:

$$\left(\frac{\partial \ln \gamma_B}{\partial m_c}\right)_{m_B} = 2\left(\frac{\partial \ln \gamma_c}{\partial m_B}\right)_{m_c} = \frac{\Delta}{m_B m_c} = f(m_B) + F(m_c). \qquad (7)$$

Even if the equation for Δ contains cross-products of m_B and m_c, the situation can still be handled [4]. Thus, if

$$\frac{\Delta}{m_B m_c} = A + B m_B + C m_c + D m_B^2 + E m_c^2 + F m_B m_c \qquad (8)$$

then

$$\left(\frac{\partial \ln \gamma_B}{\partial m_c}\right)_{m_B} = 2\left(\frac{\partial \ln \gamma_c}{\partial m_B}\right)_{m_c} = A + B m_B \\ + C m_c + D m_B^2 + E m_c^2 + \frac{4}{3} F m_B m_c \qquad (9)$$

$$\ln \gamma_B = \ln \gamma_B^\circ + m_c \left[A + B m_B + \frac{1}{2} C m_c + D m_B^2 \right. \\ \left. + \frac{1}{3} E m_c^2 + \frac{2}{3} F m_B m_c \right] \qquad (10)$$

and

$$2 \ln \gamma_c = 2 \ln \gamma_c^\circ + m_B \left[A + \frac{1}{2} B m_B + C m_c \right. \\ \left. + \frac{1}{3} D m_B^2 + E m_c^2 + \frac{2}{3} F m_B m_c \right] \qquad (11)$$

where γ_B° is the activity coefficient of glycine in a solution containing glycine only at a molality m_B and γ_c° is the activity coefficient of potassium chloride in a solution containing potassium chloride only at a molality m_c.

3. Experimental Procedure

The isopiestic apparatus was that used previously [4]. The potassium chloride was a low-bromide preparation [9] used in a previous study [10]. Glycine was recrystallized twice from a mixture of equal parts of water and ethanol, and dried in a vacuum desiccator at room temperature.

TABLE 1. *The system: water-glycine-potassium chloride at 25 °C*

$m_{ref.}$	m_B	m_c	$-\dfrac{\Delta}{m_B m_c}$	%
0.5081	0.3885	0.3073	0.161	+0.03
	.6094	.1926	.164	−.05
	.8379	.07436	.205	+.19
	.9806	----------		
0.5087	0.2350	0.3871	0.157	+0.04
	.5007	.2486	.147	−.22
	.7070	.1430	.180	−.01
	.9821	----------		
0.8178	0.6238	0.5042	0.101	−0.22
	.9712	.3292	.110	−.22
	1.3758	.1237	.132	−.02
	1.6133	----------		
0.8344	0.4470	0.6107	0.110	+0.07
	.8336	.4164	.107	−.15
	1.2486	.2065	.118	−.13
	1.6491	----------		
1.2151	0.9100	0.7731	0.0772	+0.28
	1.4412	.5116	.0722	+.02
	2.0881	.1880	.0897	+.06
	2.4548	----------		
1.2183	0.6881	0.8838	0.0786	+0.25
	1.2700	.6001	.0739	+.16
	1.7196	.3760	.0741	−.06
	2.4619	----------		
1.4380	0.4851	1.2052	0.0768	+0.23
	1.3494	0.7870	.0539	+.05
	2.1419	.3971	.0528	−.16
	2.9278	----------		
1.4461	0.3441	1.2812	0.0708	0
	1.0629	0.9340	.0558	+.03
	1.6951	.6276	.0531	+.05
	2.9454	----------		
1.6167	0.9836	1.1473	0.0477	−0.26
	2.0131	0.6521	.0436	+.10
	2.9358	.1945	.0534	−.02
	3.3151	----------		
1.6174	0.5874	1.3383	0.0562	−0.28
	1.6586	0.8245	.0437	+.05
	2.4722	.4275	.0460	+.05

B=glycine, C=potassium chloride, $m_{ref.}$ is the molality of the reference solution of potassium chloride.

4. Results

Table 1 gives the experimental data. The first column gives the molality of potassium chloride, $m_{ref.}$, in the reference solution, the second and third columns the molalities of glycine and potassium chloride, respectively, in the mixed solution in isopiestic equilibrium with the reference potassium chloride solution. The fourth column gives values of the Δ function defined by eq (5). These values have been fitted by the method of least squares to a six-parameter, quadratic equation of the form of eq (8), the numerical values of the parameters being as follows: $A = -0.2609$, $B = 0.0845$, $C = 0.2794$, $D = -0.00786$, $E = -0.10826$, $F = -0.04171$. The

[2] The cubic equation is $\Delta/(m_B m_c) = -0.32499 + 0.15795\, m_B + 0.58007\, m_c - 0.04615\, m_B^2 - 0.57817\, m_c^2 - 0.16050\, m_B m_c + 0.00653\, m_B^3 + 0.20183\, m_c^3 + 0.01798\, m_B^2 m_c + 0.08523\, m_B m_c^2$.

final column of table 1 gives the percentage change in the molality of the reference solution necessary to give Δ values in complete accord with eq (8) and the above values of the six parameters. In many cases the percentage difference is considerably greater than the experimental error in the isopiestic measurements; a ten-parameter cubic equation[2] has been tried with little better fit, and it seems likely that the surface which represents $\Delta/(m_B m_c)$ as a function of m_B and m_c is a particularly difficult one to fit to any simple equation.

5. Discussion

Table 1 contains 11 sets of data in which reference solutions of potassium chloride were equilibrated with solutions of glycine only. From these isopiestic ratios there can be calculated the osmotic coefficient of glycine solutions. The results are given in table 2 where they are compared with those calculated by the equation of Ellerton, Reinfelds, Mulcahy, and Dunlop [8]. The mean difference is 0.0007, their results in general being slightly higher.

If we insert numerical values for the parameters of eq (10), the effect of potassium chloride on the activity coefficient of glycine is given by

$$\log \gamma_B/\gamma_B^0 = m_c\{ -0.1133 + 0.03670 m_B$$
$$+ 0.06067 m_c - 0.00341 m_B^2$$
$$- 0.01567 m_c^2 - 0.01208 m_B m_c\}. \quad (12)$$

TABLE 2. *Osmotic coefficients of aqueous glycine solutions at 25 °C.*

m_B	φ^a	φ^b
0.9806	0.9314	0.9326
.9821	.9311	.9324
1.6133	.9094	.9095
1.6491	.9077	.9085
2.4548	.8898	.8917
2.4619	.8895	.8917
2.9278	.8856	.8855
2.9454	.8854	.8854
3.3151	.8822	.8817

a Present data.
b Data of Ellerton, Reinfelds, Mulcahy, and Dunlop.

Some values of $-\log \gamma_B/\gamma_B^0$ are given in table 3; it will be noted that, while the effect of potassium chloride is more pronounced when the glycine concentration is low, the effect is appreciable at all concentrations. Thus when $m_B = m_c = 1$, $-\log \gamma_B/\gamma_B^0 = 0.0471$ and as γ_B^0 is known [8] to be 0.861 at $m_B = 1$, $m_c = 0$, then $\gamma_B = 0.773$ in 1 m potassium chloride solution. This may be compared with the effect of sodium chloride on the activity coefficient of urea. At a concentration of 1 m and in the absence of sodium chloride the activity coefficient of urea is 0.922; the addition of 1 m sodium chloride lowers it to 0.898, thus $\log \gamma_B/\gamma_B^0 = -0.0113$ so that the effect is approximately four times as large with glycine.

TABLE 3. *Effect of potassium chloride on the activity coefficient of glycine in aqueous solution at 25 °C.*[a]

m_B	m_c			
	0.2	0.5	1.0	1.5
0.2	(.0191)	.0409	.0643	.0822
.5	(.0171)	.0362	.0569	.0738
1.0	.0142	.0298	.0471	(.0612)
1.5	.0116	.0243	.0390	(.0560)
2.0	.0094	.0196	(.0328)	(.0512)

a Values of $-\log \gamma_B/\gamma_B^0$ are tabulated. Values in parentheses are extrapolated.

The equation for the effect of glycine on the activity coefficient of potassium chloride becomes

$$\log \gamma_c/\gamma_c^0 = m_B\{ -0.05665 + 0.00917 m_B$$
$$+ 0.06067 m_c - 0.00057 m_B^2 - 0.02351 m_c^2$$
$$- 0.00604 m_B m_c\}. \quad (13)$$

Table 4 gives some values of $-\log \gamma_c/\gamma_c^0$ calculated by this equation. Again, the effect of glycine on the activity coefficient is large; at $m_B = m_c = 1$, $-\log \gamma_c/\gamma_c^0 = 0.0170$ and as $\gamma_c^0 = 0.604$, $\gamma_c = 0.581$ but the activity coefficient of sodium chloride, which is 0.657 when $m_B = 0$, $m_c = 1$, is reduced only to 0.650 on the addition of 1 m urea, so that $\log \gamma_c/\gamma_c^0 = -0.0043$.

TABLE 4. *Effect of glycine on the activity coefficient of potassium chloride in aqueous solution at 25 °C* [a]

m_c	m_B				
	0.2	0.5	1.0	1.5	2.0
0.2	(0.0088)	(0.0208)	0.0381	0.0524	0.0638
0.5	.0064	.0146	.0266	.0363	.0444
1.0	.0038	.0090	.0170	.0242	(.0310)
1.5	.0037	.0094	(.0190)	(.0296)	(.0412)

a Values of $-\log \gamma_c/\gamma_c^0$ are tabulated. Values in parentheses are extrapolated.

Figure 1 shows the distribution of molalities of glycine and of potassium chloride at which measurements were made in this investigation. The measurements of Roberts and Kirkwood [6] were limited to concentrations 0.5 m and less in both glycine and potassium chloride, corresponding to the rectangle on the lower left side of figure 1. It would not be expected that an equation fitted to data for comparatively high concentrations could be extrapolated to the dilute range which was the subject of the work of Roberts and Kirkwood. Nor would it be expected that their equation can be extrapolated far into the region of concentrated solutions. A fair comparison would be in the region of concentration more or less common to both sets of measurements.

This comparison can be made in two ways. In the first method, we note that Roberts and Kirkwood expressed their results by the equation

$$\ln \gamma_c = \ln \gamma_c^0 - 0.2059 m_B + 0.2824 m_B m_c^{1/2}$$
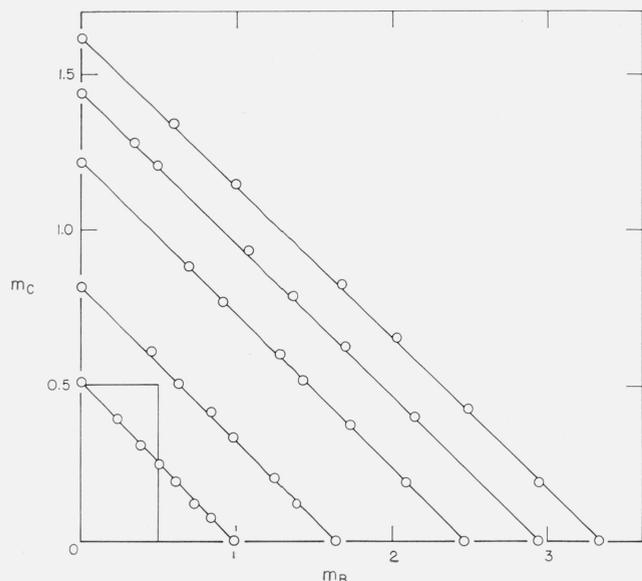$$+ 0.0247 m_B^2 - 0.1446 m_B m_c \quad (14)$$

FIGURE 1. *Isopiestic measurements.*

The rectangle at the left indicates the concentration range in which the emf measurements of Roberts and Kirkwood were made.

or

$$\frac{\Delta}{m_B m_c} = 2\left(\frac{\partial \ln \gamma_c}{\partial m_B}\right)_{m_c} = -0.4118 + 0.5648 m_c^{1/2}$$

$$+ 0.0988 m_B - 0.2892 m_c. \quad (15)$$

We calculate Δ by this equation with the molalities of the first twelve solutions of table 1; these are recorded as Δ_2 in table 5 where Δ_1 represents the values of Δ derived from the isopiestic measurements. The column headed % (1) in table 5 gives values of % copied from table 1—they are the percentage changes in the molality of the reference solution necessary to bring our isopiestic results into complete agreement with eq (8). The column headed % (2) gives the percentage change needed to bring our results into agreement with eq (15), the equation of Roberts and Kirkwood. The average values of % (1) and % (2) for the first six entries are both 0.09; this means that for the solutions of composition closest to those used by Roberts and Kirkwood, their equation, derived from emf measurements, predicts our isopiestic data with no more error than the equation we have derived from our isopiestic data. The situation is not so favorable for the next six entries, the average value of % (1) is 0.14, that of % (2) is 0.32; however, we note that not one of the points corresponding to these solutions lies in the region studied by Roberts and Kirkwood.

A second comparison can be made by using both eq (14) and eq (13) to calculate $\log \gamma_c/\gamma_c^\circ$ at selected values of m_B and m_c. The results of such calculations are shown in table 6, where pairs of values of $-\log \gamma_c/\gamma_c^\circ$ are given, the first being calculated from the emf data of Roberts and Kirkwood and the second from the present isopiestic data. A heavy line has been drawn to enclose all pairs which agree within 0.0010 or better (the average difference in this region is 0.0004). There is excellent agreement in the concentration range more or less common to both experiments. We conclude, therefore that our results are in agreement with those of Roberts and Kirkwood insofar as comparison is possible.

TABLE 5. *Comparison of isopiestic and electromotive force data*

m_B	mc	$-\Delta_1$	$-\Delta_2$	% (1)	% (2)
0.3885	0.3073	0.0192	0.0178	+0.03	+0.15
.6094	.1926	.0192	.0187	− .05	+ .05
.8379	.07436	.0128	.0122	+ .19	+ .07
.2350	.3871	.0143	.0135	+ .04	+ .09
.5007	.2486	.0183	.0190	− .22	− .08
.7070	.1430	.0182	.0171	− .01	+ .12
0.6238	0.5042	0.0317	0.0298	−0.22	+0.13
.9712	.3292	.0350	.0277	− .22	+ .50
1.3758	.1237	.0225	.0192	− .02	+ .22
0.4470	.6107	.0299	.0281	+ .07	+ .12
.8336	.4164	.0370	.0296	− .15	+ .49
1.2486	.2065	.0305	.0235	− .13	+ .47

$\Delta_1 = -55.51$ ln $a_w - m_B \varphi_B^\circ - 2$ $m_c \varphi_c^\circ$ as calculated from isopiestic measurements, Δ_2 from the emf data of Roberts and Kirkwood. %(1) is the percentage change in the molality of the reference solution required to give agreement with eq (8), %(2) that needed to give agreement with the results of Roberts and Kirkwood.

TABLE 6. *Effect of glycine on the activity coefficient of potassium chloride*

Comparison of electromotive force and isopiestic data

m_c	m_B				
	0.2	0.3	0.5	0.7	1.0
0.2	0.0090	0.0132	0.0209	0.0278	0.0365
	.0088	.0129	.0208	.0277	.0381
0.3	0.0078	0.0113	0.0178	0.0235	0.0304
	.0080	.0115	.0186	0.249	.0337
0.5	0.0064	0.0093	0.0144	0.0186	0.0234
	.0064	.0091	.0146	.0194	.0266
0.7	0.0057	0.0083	0.0127	0.0163	0.0201
	.0049	.0073	.0117	.0157	.0214
1.0	0.0055	0.0079	0.0121	0.0155	0.0189
	.0038	.0056	.0090	.0123	.0170

$-\log \gamma_c/\gamma_c^\circ$ is tabulated. The first (upper) of each pair of figures is the value calculated from the emf data of Roberts and Kirkwood, the second (lower) that from the present isopiestic data.

6. Solubility Relations

By evaporation to dryness in vacuo at room temperature of a saturated solution of glycine in water, the solubility of glycine in water at 25 °C was found to be 3.337 mole/kg of water. McMeekin, Cohn, and Weare [11] found 2.886 mole/liter of solution or 3.331 mole/kg of water. The equation of Ellerton, Reinfelds, Mulcahy, and Dunlop [8] gives 0.7300 for the activity coefficient of glycine in water at this concentration. Hence the solubility product is 2.436 mole/kg. Putting $m_c = 0.5$ mole/kg, a short series of approximations shows that eq (10) is satisfied by $m_B = 3.437$ mole/kg, $\gamma_B = 0.7088$, $m_B \gamma_B = 2.436$ mole/kg. Thus we predict a solubility of 3.437 mole/kg in a 0.5 m potassium chloride

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solution. Again by evaporation to dryness of a saturated solution of glycine in 0.5 m potassium chloride solution, we found a solubility of 3.442 mole/kg.

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7. References

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