Salt Effects in Vapor-Liquid Equilibrium: Testing the Thermodynamic Consistency of Ethanol-Water Saturated with Inorganic Salts

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A semi-empirical test for the thermodynamic consistency of isobaric liquid-vapor equilibrium data for ethanol-water saturated with a salt is proposed. The test is based upon an adaptation of the Herington method (*1*) in which the ternary system is treated as a special binary. The test is applied both to full concentration range data and to data which are incomplete at the high alcohol end. For data which are incomplete at the high water end, a less severe test is employed.

Literature data for 23 systems composed of ethanol, water, and an inorganic salt at saturation were tested. By the criterion of the proposed test, fourteen were deemed consistent, six were borderline, and three were pronounced inconsistent.

All consistent isobaric liquid-vapor equilibrium data must satisfy the equation

$$\int_0^1 \left[\log \frac{\gamma_1}{\gamma_2} - \frac{H^M}{2.303RT^2} \left(\frac{dT}{dx} \right) \right] dx = 0 \quad (1)$$

Generally heat of mixing data are unavailable, and so for binary isobaric systems Herington (*1*) suggested a semi-empirical procedure in which the area above and the area below the abscissa are measured, the areas (Σ) are summed and are subtracted one from the other (I). The percentage deviation is defined as

$$D = \frac{100\, I}{\Sigma} \quad (2)$$

Herington showed that if

$$J - |D| > 0 \quad (3)$$

the data are consistent.[*] J is defined as

$$J = \frac{150\, |\theta|}{T_{\text{min}}} \quad (4)$$

The only previous attempt to test systems containing two liquids and a salt was by the "slope" method. Kogan (*2*) has compared the observed slope of the activity coefficient of the less volatile liquid component with the calculated slope making use of the equation

$$\ln\gamma_j = - \int_0^x \frac{x_i}{1 - x_i}\, d\ln\gamma_i + C \quad (5)$$

The calculated and experimental values should lie on two parallel curves. The method was tested by Kogan on isobaric data for three systems containing ethanol, water, and a salt at saturation. The biggest drawback of the "slope" method is that it is insensitive. An alternative method is presented for testing the consistency of salt data which is based upon Herington's test.

METHOD OF TESTING ISOBARIC SALT DATA

The method makes the basic assumption that the ternary system can be treated as a binary composed of ethanol saturated with salt as one component and water saturated with salt as the other component. When these two solutions are mixed it is found in every case that, where the solubility of the salt in the boiling alcohol-water mixtures has been measured, precipitation occurs and hence the final solution is always saturated with salt. The activity coefficients of ethanol and water are calculated from Equation (6):

$$\ln\gamma_i = \ln \left(\frac{y_i \Pi}{x_i p_i^0} \right) + (B_{ii} - V_i)(\Pi - p_i^0)/RT \quad (6)$$

with one modification. The saturation vapor pressure p_i^0 is not applicable when the solvent is saturated with salt. Instead, for water the vapor pressure of the saturated salt solution p_2' is substituted for p_2^0. For ethanol these vapor pressures are not available and so a correction to the saturation vapor pressure is applied by multiplying by the ratio of the vapor pressure of ethanol saturated with salt Π_T to the vapor pressure of pure ethanol p_{1T}^0 at the salt solution boiling point. This ratio ϵ is assumed independent of temperature. Incomplete data are treated somewhat differently than complete data and so each will be considered separately.

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[*] Herington takes the absolute value of I in Equation (2) rather than of D in Equation (3).

Complete Data

Log (γ_1/γ_2) is plotted against x and the areas above and below the abscissa are measured. These areas will not generally be identical because the heat of mixing [see Equation (1)] is unknown. The heat of mixing will be a composite quantity which will include a term due to the precipitation of the salt. Before the Herington test can be applied to the present data it is desirable to ensure that the heat of mixing with and without salts is of the same order of magnitude. By using the Wilson equation (*3*) to fit the excess free energies and by assuming that the energy terms $(g_{ij} - g_{ii})$ are independent of temperature, it can be shown that

$$H^M = x(1-x)$$

$$\left\{ \frac{(1-A_{21})(g_{21}-g_{11})}{1-A_{21}(1-x)} + \frac{(1-A_{12})(g_{12}-g_{22})}{1-A_{12}x} \right\} \tag{7}$$

Orye and Prausnitz (*4*) have stated that Equation (7) gives a reasonable but rough estimate of the heat of mixing, particularly for nonassociated solutions. Comparison of the calculated values for the ethanol-water system itself (*5, 6*) with the system containing a wide variety of salts showed that there was only some 20% difference. After due allowance is made for the uncertainties in the calculated values, the result would suggest that the Herington test can safely be applied to the present salt data and the sign of $(J - |D|)$ used to decide if the data are consistent.

When the theoretical derivation of the Herington test is examined it is found that J was calculated on the largest value of $(|\Delta H^M{}_{\text{Max}}|/|\Delta G^E{}_{\text{Max}}|)$ for 15 widely assorted binary systems. The largest value of the ratio was 2.9 whereas the value for ethanol-water was only 0.6. Herington's value of 3.0 seems somewhat unrealistic in the present case but 0.6 would not reflect the uncertainties caused by the addition of salt to the ethanol-water system. An arbitrary value of 1.5 was chosen to give a more severe test of consistency. This yields

$$K = \frac{75\,|\theta|}{T_{\text{min}}} \tag{8}$$

Consistent data should satisfy Equation (3) and Equation (9)

$$(K - |D|) > 0 \tag{9}$$

Incomplete Data

Some of the salt data in the literature do not cover the entire liquid composition range. For such systems the restricted range area tests (*7*) can be applied. Figure 1 shows a typical case where the data are incomplete, area FGCD should differ from area EBHK by the corresponding heat of mixing term.

$$\int_0^{\log \gamma_1'} x\, d\log \gamma_1 - \int_{\log \gamma_2'}^{\log \gamma_2''} (1-x)\, d\log \gamma_2 + \int_{T_1}^{T'} \frac{H^M}{2.303RT^2}\, dT = 0 \tag{10}$$

The value of the second integral is subtracted from the value of the first integral in Equation (10) to give the difference I_R. Summation of the areas requires a correction before D_R can be calculated. In order to apply the Herington test to a graph of log γ_1 and log γ_2 versus x rather than to a graph of $\log(\gamma_1/\gamma_2)$ versus x it is necessary to subtract twice the common area HBJ (Figure 1) from the sum of the areas. The value of J_R is calculated from the equation:

$$J_R = \frac{150\,|\theta_R|}{T_{\text{min}}} \tag{11}$$

where θ_R is the difference in boiling points over the restricted range of x. The condition for thermodynamic consistency is

$$J_R - |D_R| > 0 \tag{12}$$

In the case of data which are incomplete at low x, θ_R is small and so J_R is small, and Equation (12) becomes a severe test of consistency. However for data which are incomplete at high x, θ_R is little different from θ and so a more severe second test is applied

$$K_R = \frac{75\,|\theta_R|}{T_{\text{min}}} \tag{13}$$

and for consistency

$$K_R - |D_R| > 0 \tag{14}$$

APPLICATION

The tests developed in the preceding section can be applied to any salt system provided the activity coefficients are based upon the standard state of each liquid component saturated with salt. Here we shall test the ethanol-water system which has been saturated in turn with each of a wide range of inorganic salts. Interpolation of literature data yielded the required values of the vapor pressure of water (*8*) and ethanol (*9*), the molar volumes of the two liquids (*10*), and the second virial coefficients of water (*11*), and ethanol (*12*).

Complete Data

The following example illustrates how the test is applied to the specific case of sodium chloride.

The optimum values of m and c in Equation (15) are obtained using vapor pressure data (*8, 13*)

$$\log p_2' = m \log p_2^0 - c \tag{15}$$

It has been found (*14*) that under 755 mm. Hg pressure ethanol saturated with sodium chloride boils at 77.7°C. at which temperature the vapor pressure of pure ethanol is 741.1 mm. Hg (*9*).
Hence

$$\epsilon = \frac{755}{741.1} = 1.019$$

The activity coefficients are calculated and the results

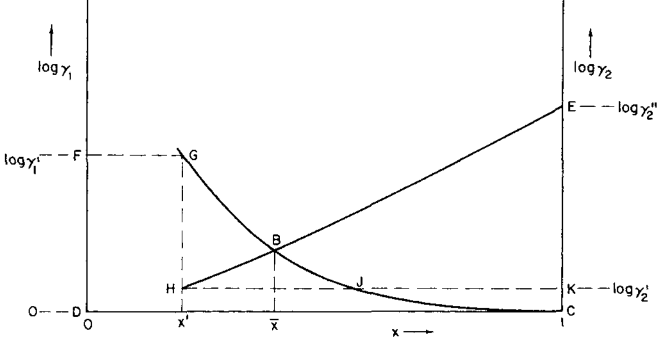

Fig. 1. Restricted range area test.

shown graphically (see Figure 2). That the log γ_2 curve goes through the origin is satisfactory in view of the use of independent vapor pressure data. (This condition is fulfilled for all 21 systems examined.) From a graph of $\log(\gamma_1/\gamma_2)$ versus x we find an above and below the abscissa area of 0.1751 and 0.1903 respectively, and so $D = -4.1\%$, $\theta = 31.1°C.$, $J = 13.3$ and $K = 6.7$. These results satisfy Equations (3) and (9).

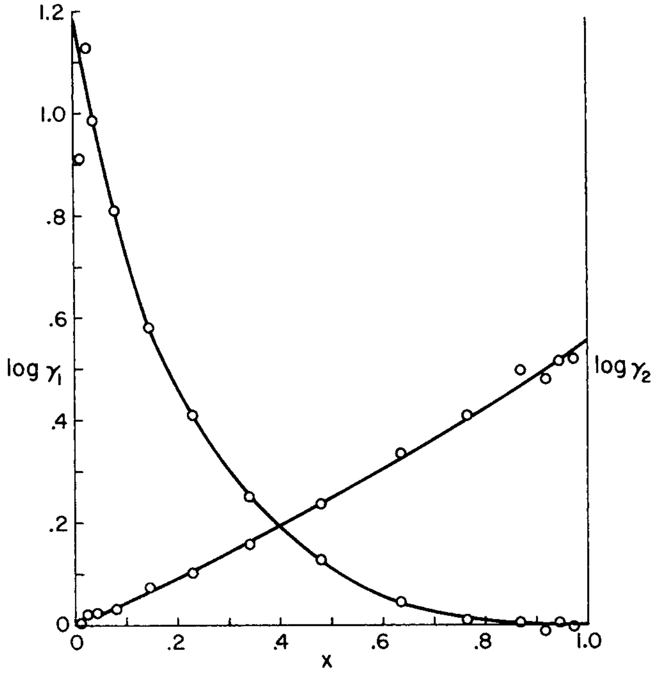

Fig. 2. Ethanol-water saturated with sodium chloride *(14)*.

This method has been applied to sixteen systems and the results are shown in Table 1. Systems 1 to 3, 6 to 8, 10 to 12, and 16 satisfy both conditions and it appears safe to assume that they are thermodynamically consistent. Systems 4, 9, and 13 are borderline cases and no firm conclusion can be drawn. Systems 5, 14, and 15 fail both conditions and it appears reasonable to doubt their consistency.

The result for sodium iodide (system 5) is not unexpected. The boiling point graph and the log γ_1 versus x graph show unusual curvature in the x-range 0.6-0.95. A change in the value of ϵ would not remove the curvature.

Incomplete Data

The results of calculations for seven systems are given in Table 2. For the systems which are incomplete at high alcohol concentration, 2 to 5 and 7, we can apply Equations (12) and (14). Systems 3, 5, and 7 satisfy both equations and are deemed consistent. No firm conclusions can be drawn about 2 and 4 which satisfy one condition only.

Before discussing the two systems which are incomplete at low alcohol concentration, it is instructive to apply Equation (12) to the 0.2-1.0 x region of the 15 systems for which complete data are available. These results are shown in Table 3. Systems 1 to 10 were deemed consistent over the whole range but five of them fail to satisfy Equation (12). One of the three borderline cases (systems 11 to 13), and both inconsistent sets of results (systems 14 and 15) fail to satisfy Equation (12). The reason for this apparent contradiction lies in the narrow temperature range involved and the corresponding small value of J_R. If all the errors in measurement are lumped together in x and an error of ± .005 is assumed for the full range data

TABLE 1. APPLICATION OF THE TEST TO COMPLETE DATA

System	Salt	m	c	ϵ	D	J	$(J - \lvert D\rvert)$	$(K - \lvert D\rvert)$
1	NH_4Cl *(14)*	0.9294	−0.0032	1.013	− 5.0	16.5	11.5	3.3
2	$(NH_4)_2SO_4$ *(14)*	0.9731	0.0487	1.011	− 2.5	13.1	10.6	4.1
3	NaCl *(14)*	0.9935	0.1109	1.019	− 4.1	13.3	9.2	2.6
4	NaBr *(15)*	0.9174	0.0776	0.912	−14.3	16.3	2.0	− 6.1
5	NaI *(15)*	0.9606	0.4820	0.786**	−31.2	25.1	− 6.1	−18.6
6	$NaNO_3$ *(14)*	0.8853	−0.0704	1.020	− 7.4	19.0	11.6	2.1
7	KCl *(14)*	0.9547	−0.0037	1.000	− 1.8	13.3	11.5	5.9
8	KBr *(15)*	0.9572	0.0360	0.983	− 6.2	14.4	8.2	1.0
9	KI *(15)*	0.9383	0.0719	0.886	−10.5	15.7	5.3	− 2.6
10	K_2SO_4 *(14)*	0.9962	0.0105	1.023	− 4.9	10.2	5.3	0.2
11	$Ca(NO_3)_2$ *(16)*	1.0712	0.9368	0.747	− 5.3	27.3*	22.0	8.3
12	$Ba(NO_3)_2$ *(14)*	1	0	1.027	− 3.8	10.1	6.3	1.3
13	CuCl *(14)*	1	0	1.042	− 5.4	9.7	4.3	− 0.5
14	$HgCl_2$ *(14)*	1	0	0.892	−12.0	8.1	− 3.9	− 7.9
15	$HgBr_2$ *(14)*	1	0	0.965	−11.0	8.9	− 2.1	− 6.5
16	HgI_2 *(14)*	1	0	1.010	− 0.9	9.4	8.5	3.8

* Estimated value.
** Approximate value (see text).

TABLE 2. APPLICATION OF THE TEST TO INCOMPLETE DATA

System	Salt	Range of x values	m	c	ϵ	D_R	J_R	$(J_R - \lvert D_R\rvert)$	$(K_R - \lvert D_R\rvert)$
1	LiCl*(17)*	0.3-1.0	0.9659	0.9199	0.4920	7.9	4.0	−3.9	—
2	NaF *(18)*	0-0.8	1	0	1	8.7	9.6*	0.9	−3.9
3	NaCl *(18)*	0-0.8	0.9935	0.1109	1.019	6.5	13.2	6.7	0.1
4	Na_2SO_4 *(19)*	0-0.8	1.019	0.0969	1.000	−5.8	9.4	3.6	−1.1
5	KCl *(18)*	0-0.8	0.9547	−0.0037	1.000	−5.0	13.2	8.2	1.6
6	KI *(17)*	0.2-1.0	0.9383	0.0719	0.9750	2.1	2.5	0.4	—
7	$BaCl_2$ *(16)*	0-0.6	0.9906	0.0348	1	0.5	10.3*	9.8	4.7

* Estimated value.

TABLE 3. COMPARISON OF THE TESTS FOR COMPLETE AND INCOMPLETE DATA

System	Salt	D_R	J_R	$(J_R - \|D_R\|)$*	$(J - \|D\|)$	$(K - \|D\|)$
1	NH_4Cl (*14*)	− 3.7	2.0	−1.7	11.5	3.3
2	$(NH_4)_2SO_4$ (*14*)	− 0.3	1.4	1.1	10.6	4.1
3	NaCl (*14*)	3.0	1.2	−1.8	9.2	2.6
4	$NaNO_3$ (*15*)	− 0.7	1.0	0.3	11.6	2.1
5	KCl (*14*)	8.1	1.2	−6.9	11.5	5.9
6	KBr (*14*)	− 9.1	2.0	−7.1	8.2	1.0
7	K_2SO_4 (*15*)	0.9	2.0	1.1	5.3	0.2
8	$Ca(NO_3)_2$ (*15*)	− 2.9	6.8	3.9	22.0	8.3
9	$Ba(NO_3)_2$ (*14*)	− 4.5	2.1	−2.4	6.3	1.3
10	HgI_2 (*16*)	− 2.0	2.2	0.2	8.5	3.8
11	NaBr (*14*)	− 1.8	2.5	0.7	2.0	−6.1
12	KI (*14*)	0.4	2.8	2.4	5.3	−2.6
13	CuCl (*14*)	− 5.8	2.1	−3.7	4.3	−0.5
14	$HgCl_2$ (*14*)	−11.6	1.9	−9.7	− 3.9	−7.9
15	$HgBr_2$ (*14*)	− 7.1	1.9	−5.2	− 2.1	−6.5

* Range: $x = 0.2\text{-}1.0$.

of sodium chloride $D = -4.1 \pm 4.7$.

Hence it would appear reasonable to accept that consistent data will satisfy Equation (12) and pronounce system 6 of Table 2 consistent but to reserve judgment about system 1 until a full range of data is available.

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NOTATION

A_{21}, A_{12} = constants in the Wilson equation
B_{ii} = second virial coefficient of component i
c = empirical constant
C = integration constant
D = percentage deviation: $(100\ I/\Sigma)$
$(g_{ij} - g_{ii})$ = energy terms related to A_{ij}
$\Delta G^E{}_{\text{Max}}$ = the maximum value of the excess free energy of mixing
H^M = heat of mixing
$\Delta H^M{}_{\text{Max}}$ = the maximum value of the heat of mixing
I = difference between the area above and below the abscissa
J = $(150\ |\theta|/T_{\min})$
K = $(75\ |\theta|/T_{\min})$
ln = natural logarithm
log = logarithm to the base 10
m = empirical constant
p_i^0 = saturation vapor pressure of component i
p_2' = vapor pressure of water saturated with salt
R = gas constant
T = temperature in °K.
$T_{\min}$ = lowest boiling point in the system
V_i = molar volume of component i
x = mole fraction of ethanol in the liquid phase on a salt-free basis
x_i = mole fraction of component i in the liquid phase on a salt-free basis
y_i = mole fraction of component i in the vapor phase

Greek Letters

γ_i = activity coefficient of component i
ϵ = $\Pi_T/p_{1T}{}^0$
θ = difference between maximum and minimum boiling points
Π = total pressure
Σ = total area irrespective of the sign of the integrals

Subscripts

1 = ethanol
2 = water
R = restricted area
T = fixed temperature

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