Testing the Thermodynamic Consistency of Methanol-, 1-Propanol-, and 2-Propanol-Water Systems Saturated with Salts

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Recently Jaques and Furter (1972) described a method of testing the thermodynamic consistency of isobaric liquid-vapor equilibrium data for ethanol-water saturated with inorganic salts. Because heats of mixing were unavailable, an adaptation of the method of Herington (1951) for salt-free data was employed. The testing procedure assumes that the ternary system can be treated as a binary composed of alcohol saturated with salt as one component and water saturated with salt as the other component. The activity coefficient of alcohol and water are calculated from Equation (1)

$$\ln \gamma_i = \ln (y_i \Pi / x_i\, p_i^1) + (B_{ii} - V_i)(\Pi - p_i^1)/RT \quad (1)$$

When available the vapor pressure of solvent saturated with salt over a temperature range is used in Equation (1). Otherwise the ratio of the vapor pressure of solvent saturated with salt to the vapor pressure of pure solvent at the salt solution boiling point is assumed independent of temperature, and the required solution vapor pressure is calculated from that of the pure solvent.

Consistent data should satisfy Equation (2) and (3)

$$J - |D| > 0 \quad (2)$$

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

The test has now been applied to methanol-water, 1-propanol-water and 2-propanol-water systems each saturated with one of several inorganic salts.

RESULTS AND DISCUSSION

Interpolation of literature data yielded the required values of the vapor pressure of water, methanol, and 1-propanol (Prausnitz et al., 1967), and 2-propanol (Hala et al., 1968); the molar volumes of water, methanol, and 1-propanol (Prausnitz et al., 1962), and 2-propanol (Timmermans, 1950); and the second virial coefficient of water and methanol (Rowlinson, 1949) and 1- and 2-propanol (Cox, 1961). The *International Critical Tables* (1929) provided data on the temperature-dependence of the vapor pressure of water saturated with all salts except mercuric chloride and lead nitrate. The boiling point of methanol saturated with the four salts marked with an asterisk in Table 1 were not measured by Meranda and Furter (1972) and hence their values were estimated by extrapolation of the boiling point—liquid composition data for each salt. This allowed calculation of both ϵ and J.

The method has been applied to eleven methanol-water systems and the results are shown in Table 1. Systems 1 to 3, 6, and 7 satisfy Equations (2) and (3) and it appears safe to assume that they are thermodynamically consistent. Systems 4 and 8 fail both conditions and their consistency is in doubt. As systems 5 and 9 to 11 satisfy Equation (2) only they are regarded as borderline cases and hence no definite conclusion can be drawn.

For the seven 1-propanol-water systems of Table 2, the test indicates that 1, 3, 4, and 6 are consistent, 2 appears to be inconsistent whereas 5 and 7 are borderline cases.

The results for the two 2-propanol-water systems are given in Table 3. System 1 is clearly consistent as it satisfied Equations (2) and (3). The data for calcium nitrate only cover the alcohol mole fraction from 0.2 to 1.0. For this system the restricted range area test (Herington, 1968) was applied (See Figure 1). However, in the case of data which are incomplete at low x, θ_R is small and so J_R is small and Equation (2) becomes a severe test of consistency. The satisfaction of Equation (2) would indicate consistency, but the failure in the case of calcium nitrate is inconclusive. A full range of data are required before a final judgment can be made.

NOTATION

B_{ii} = second virial coefficient of component i
c = empirical constant used in equation: $\log p_2^1 = m \log p_2^0 - c$
D = percentage deviation, $(100\, I/\Sigma)$
I = difference between the area above and below the abscissa
J = $(150|\theta|/T_{\min})$

TABLE 1. APPLICATION OF THE TEST TO METHANOL-WATER SYSTEMS

System	Salt	m	c	ϵ	δ	D	J	$(J - \|D\|)$	$(K - \|D\|)$
1	—[a]	—	—	—	—	7.7	15.8	8.1	0.2
2	NH_4Cl[a]	0.9294	−0.0032	1.010	—	−3.0	22.9	19.9	8.5
3	NaCl[a]	0.9935	0.1109	1.032	—	−2.5	19.8	17.3	7.4
4	NaBr[b]	0.9174	0.0776	0.791*	—	−40.3	21.0	−19.3	−29.8
5	NaI[b]	0.9606	0.4820	0.476*	—	−22.7	23.7	1.0	−10.8
6	$NaNO_3$[a]	0.8853	−0.0704	1.008	—	−5.8	25.4	19.6	6.9
7	KCl[a]	0.9547	−0.0037	1.045	—	2.9	20.0	17.1	7.1
8	KBr[b]	0.9572	0.0360	0.877*	—	−26.7	19.6	−7.1	−16.9
9	KI[b]	0.9383	0.0719	0.805*	—	−16.4	21.0	4.6	−5.9
10	$HgCl_2$[a]	1	0	0.795	—	−6.3	8.3	2.0	−2.1
11	$Pb(NO_3)_2$[a]	—	—	1.018	0.875	−16.0	17.5	1.5	−7.2

[a] Johnson and Furter, 1960.
[b] Meranda and Furter, 1972.
* Estimated values (see text).

TABLE 2. APPLICATION OF THE TEST TO 1-PROPANOL-WATER SYSTEMS (JOHNSON AND FURTER, 1960)

System	Salt	m	c	ϵ	δ	D	J	$(J-\lvert D\rvert)$	$(K-\lvert D\rvert)$
1	—	—	—	—	—	1.3	5.2	3.9	1.3
2	NH_4Cl	0.9294	−0.0032	1.009	—	−15.2	11.0	−4.2	−9.7
3	NaCl	0.9935	0.1109	1.008	—	−0.2	8.4	8.2	4.0
4	$NaNO_3$	0.8853	−0.0704	1.008	—	0.4	13.9	13.5	6.6
5	KCl	0.9547	−0.0037	1.008	—	−8.4	8.5	0.1	−4.1
6	$HgCl_2$	1	0	0.867	—	2.1	4.5	2.4	0.2
7	$Pb(NO_3)_2$	—	—	1.015	0.875	−3.5	6.5	3.0	−0.2

TABLE 3. APPLICATION OF THE TEST TO 2-PROPANOL-WATER SYSTEMS

System	Salt	m	c	ϵ	δ	D	J	$(J-\lvert D\rvert)$	$(K-\lvert D\rvert)$
1	—[a]	—	—	—	—	0.3	8.4	8.1	3.9
2	$Ca(NO_3)_2$*[b]	1.0712	0.9368	0.964	—	7.0†	3.0†	−4.0†	—

[a] Kohoutova et al., 1970.
[b] Ciparis, 1966.
* Range: $x = 0.2 - 1.0$.
† Restricted area values.

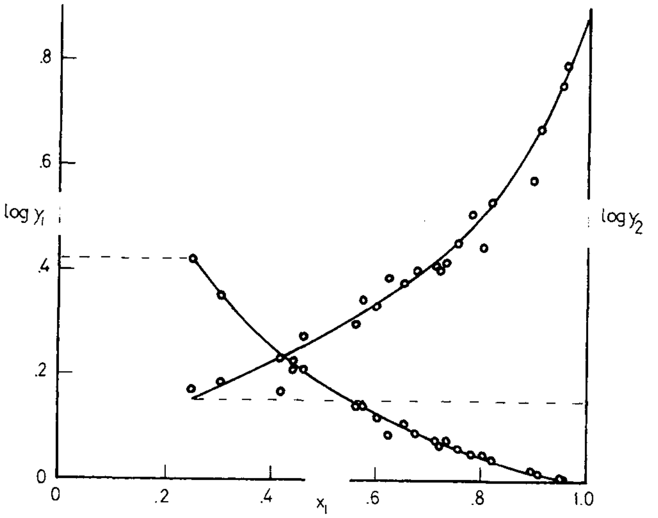

Fig. 1. 2-Propanol-water saturated with calcium nitrate (Ciparis, 1966).

K = $(75|\theta|/T_{\min})$
ln = natural logarithm
log = logarithm to the base 10
m = empirical constant (see c)
p_i^1 = vapor pressure of component i saturated with salt
p_2^0 = saturation vapor pressure of water
R = gas constant
T = temperature in °K
$T_{\min}$ = lowest boiling point in system
V_i = molar volume of component i
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
δ, ϵ = ratio of vapor pressure of solvent saturated with salt to the vapor pressure of pure solvent at the salt solution boiling point for water and alcohol respectively
θ = difference between maximum and minimum boiling point
Π = total pressure
Σ = total area irrespective of the sign of the integrals

Subscripts

1 = alcohol
2 = water
R = restricted area

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