Salt Effect in Vapor-Liquid Equilibria of Methanol–Ethyl Acetate–Calcium Chloride System

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To present the characteristics of the salt effect, vapor-liquid equilibrium relationships in the methanol–ethyl acetate–calcium chloride system at atmospheric pressure were determined. The effect of various concentrations of calcium chloride on the relative volatilities of methanol with respect to ethyl acetate is shown. The solubilities of calcium chloride in boiling methanol–ethyl acetate liquid were also determined. From the solubility data, it is assumed that methanol forming a solvate of $CaCl_2 \cdot 6CH_3OH$ is trapped by calcium chloride and cannot easily evaporate.

This research was undertaken as a continued study of the phase equilibria of systems involving salts (5–7). While the salt effects in vapor-liquid equilibria have been well documented for systems containing water (*3*, *4*), data on nonaqueous systems are scarce (*1*, *5*). The methanol–ethyl acetate–calcium chloride system was chosen to obtain additional information. The salt chosen is soluble in methanol, but sparingly soluble in ethyl acetate.

Isobaric vapor-liquid equilibrium data at atmospheric pressure are reported for the above-mentioned system with 5, 10, 15, and 20% calcium chloride and saturated with calcium chloride. The solubility of calcium chloride in the boiling methanol–ethyl acetate system was determined graphically. The interaction between calcium chloride and methanol was studied quantitatively on the solubility. We took into account that methanol solvates with calcium chloride to make $CH_3OH \cdot 6CaCl_2$ and that one methanol molecule and two ethyl acetate molecules are clustered.

EXPERIMENTAL

The equilibrium still was a modification of the Othmer type employed by Johnson and Furter (*4*). To heat it, a wall electric heater regulated by a transformer was substituted for a gas burner. The liquid phase was stirred by a magnetic stirrer. The temperatures of the boiling liquid and the vapor phase were measured with two mercury-in-glass thermometers with a range of 50° to 100° C, and 0.1° C divisions. These thermometers had been checked at 60°, 70°, 80°, 90°, and 100° C against a mercury-in-glass thermometer certified by the National Research Laboratory of Metrology.

The procedure, that of Johnson and Furter (*4*), is discussed elsewhere (*5*). Within the limits of our apparatus, the salt, being almost completely nonvolatile, appeared only in the liquid phase. Only the equilibrium vapor condensate samples were analyzed. The concentrations of the equi-

Table I. Vapor-Liquid Equilibrium Data of Methanol–Ethyl Acetate System at 1 Atm

x_1	y_1	t	x_1	y_1	t
0.000	0.000	77.1	0.497	0.604	63.6
0.018	0.091	75.1	0.630	0.670	63.0
0.086	0.284	71.5	0.725	0.725	62.8
0.138	0.361	69.9	0.800	0.770	63.0
0.195	0.402	68.2	0.898	0.848	63.6
0.263	0.460	66.4	0.952	0.912	63.8
0.382	0.539	64.4	1.000	1.000	64.8

Table II. Vapor-Liquid Equilibrium Data of Methanol–Ethyl Acetate–$CaCl_2$ System at 1 Atm

x'_1	y'_1	t
5 Wt % $CaCl_2$		
0.500	0.550	64.7
0.599	0.600	63.8
0.702	0.662	62.9
0.800	0.728	63.5
0.900	0.814	63.7
0.951	0.890	64.5
1.000	1.000	65.3
10 Wt % $CaCl_2$		
0.651	0.579	64.0
0.702	0.608	63.5
0.902	0.788	64.2
0.950	0.870	65.0
1.000	1.000	66.2
20 Wt % $CaCl_2$		
0.803	0.604	64.1
0.951	0.842	65.4
0.981	0.923	67.9
1.000	1.000	69.5
25 Wt % $CaCl_2$		
0.873	0.656	65.3
0.925	0.759	66.0
0.951	0.816	68.0
1.000	1.000	71.7
Saturated $CaCl_2$		
0.000	0.000	77.3
0.075	0.245	72.5
0.197	0.378	68.9
0.299	0.450	66.9
0.377	0.506	65.7
0.497	0.533	65.2
0.521	0.541	64.9
0.576	0.546	64.7
0.601	0.546	65.0
0.626	0.556	64.9
0.702	0.552	64.8
0.804	0.567	65.6
0.904	0.662	67.9
0.948	0.769	70.9
1.000	1.000	76.2

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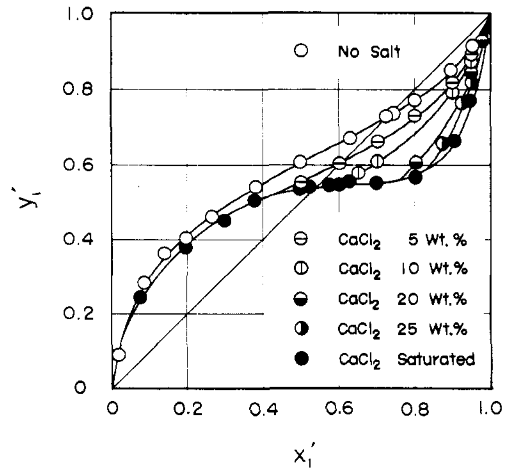

Figure 1. Vapor-liquid equilibrium curves for methanol–ethyl acetate-calcium chloride system at 1 atm

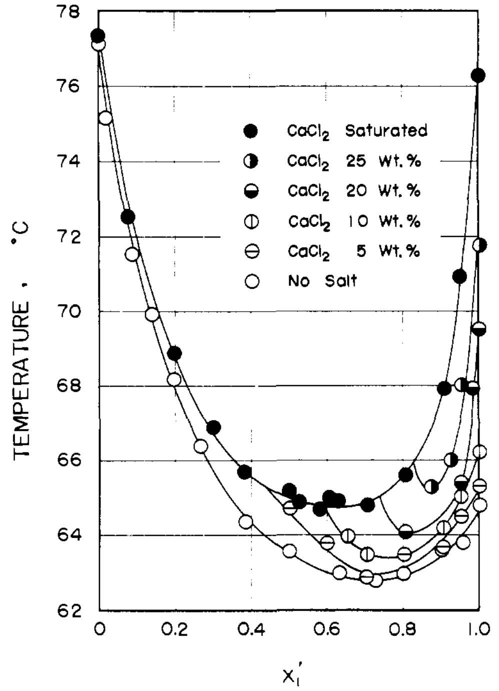

Figure 2. Boiling points of methanol–ethyl acetate-calcium chloride system at 1 atm

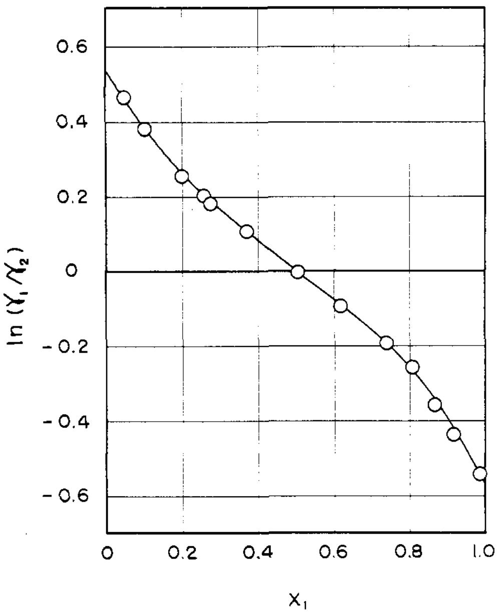

Figure 3. Diagram of ln (γ_1/γ_2) vs. molar composition for thermodynamic consistency test of methanol (1)–ethyl acetate (2) system at 1 atm

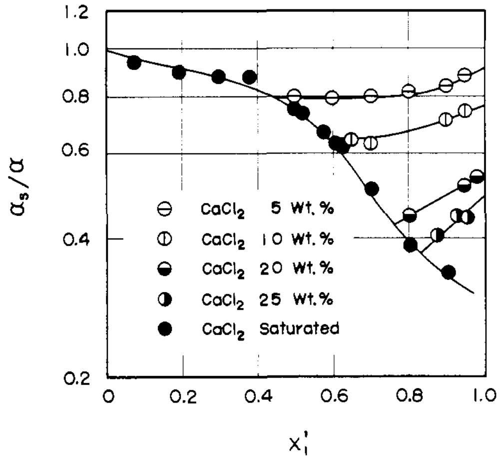

Figure 4. Diagram of ln salt effect vs. molar composition of methanol–ethyl acetate-calcium chloride system at various salt concentrations at 1 atm

librium liquid phase were calculated from the mass balance and the analyzed concentrations of the vapor phase. The holdup in the vapor phase chamber and condenser was neglected, because the uncertainty is at most 0.0003 mole fraction, which is within the error of measurement. The vapor condensate sample was analyzed by means of refractive index measurements at 20° C. An Abbe refractometer was used.

The liquid samples employed were purified by repeated distillation through an Oldershaw column (50-mm i.d. and 50 stages). The final purified samples gave no trace of impurity peaks with a Beckman Instruments GC-2A gas chromatograph, using a 6-ft column of 10% dioctyl sebacate–2% sebacic acid on Celite 545.

RESULTS AND DISCUSSION

The experimental vapor-liquid equilibrium data are presented in Tables I and II. Table I indicates the result when no salt was present; Table II, when salt was present. Figures 1 and 2 show $x - y$ and $t - x$ plots, respectively. The methanol–ethyl acetate system forms an azeotrope whose composition is 0.725 mole fraction of methanol. Figure 3 shows log (γ_1/γ_2) *vs.* x_1 plots for the system. Its thermodynamic consistency was checked by Herington's (*2*) area test. The result is

$$D < J \quad (D = 2.35, J = 6.39)$$

Since calcium chloride is sparingly soluble in ethyl acetate but soluble in methanol, the volatility of methanol relative to ethyl acetate is decreased by adding salt to the volatile binary system. In Figure 1, the azeotropic point decreases from 0.725 to 0.542 mole fraction of methanol. The higher the concentration of salt, the greater is the salt effect. The plot of relative volatility ratio (α_s/α) of methanol to ethyl acetate *vs.* x_1 is shown in Figure 4.

Each salt concentration at the intersection of curves of constant salt concentration to salt-saturation shows the solubility of calcium chloride in the volatile binary system. The solubilities thus obtained (Figure 5) are linear. From

Table III. Predicted Values of Salt Effect

x_1'	$N_3/100$	x_{1a}'	y_1' calcd	y_1' obsd	Error, %
		5 Wt % $CaCl_2$			
0.50	0.028	0.397	0.549	0.547	0.4
0.60	0.025	0.520	0.613	0.600	2.2
0.70	0.023	0.650	0.680	0.660	3.0
0.80	0.020	0.772	0.750	0.725	3.4
0.90	0.017	0.889	0.883	0.822	7.4
		Saturated $CaCl_2$			
0.50	0.035	0.352	0.527	0.536	1.7
0.60	0.060	0.354	0.524	0.545	2.2
0.70	0.080	0.375	0.535	0.550	2.7
0.80	0.100	0.400	0.500	0.515	2.9
0.90	0.120	0.450	0.653	0.580	12.6

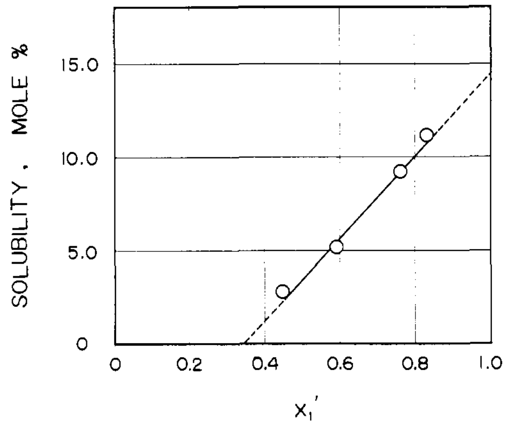

Figure 5. Salt effect vs. calcium chloride concentration

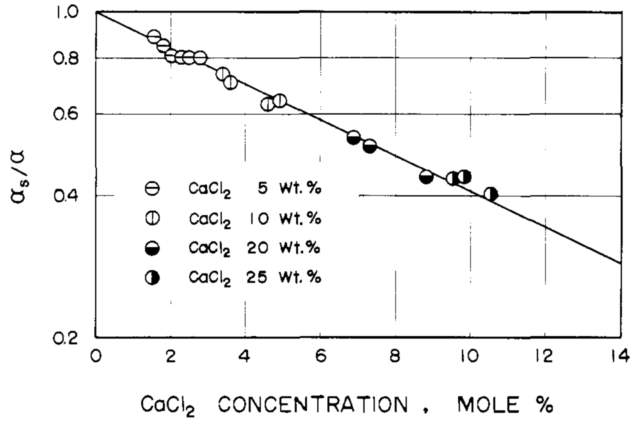

Figure 6. Solubility of calcium chloride in boiling methanol–ethyl acetate mixture at 1 atm

0 to 0.333 mole fraction of methanol, the solubility is almost equal to zero. These solubility data indicate that, if calcium chloride is dissolved only by the methanol contained in the methanol and ethyl acetate solutions, both solvents exist in the form of clustered molecules comprising one methanol molecule and two ethyl acetate molecules. It may be assumed that, in methanol concentration over 0.333 mole fraction, free molecules forming nonclustered molecules are present in the system, so that the salt is dissolved in the free molecules of methanol. From the extrapolated solubility (mole ratio of calcium chloride to methanol, approximately 1 to 6), calcium chloride and methanol are believed to form a solvate of $CaCl_2 \cdot 6CH_3OH$. Methanol forming a $CaCl_2 \cdot 6CH_3OH$ solvate may be said to be trapped by calcium chloride and cannot easily evaporate. Hence, the vapor pressure of methanol drops to a corresponding level.

The salt effect is predicted by the above mechanism. The active concentration of methanol in the liquid phase is given by the equation

$$x_{1a}' = \frac{x_1' - N_{s1}}{(x_1' - N_{s1}) + x_2'} \tag{1}$$

The vapor-phase concentration will correspond at y_1' to $x_1' = x_{1a}'$ when no salt is present (Table III).

The data agree with the semitheoretical equation proposed by Johnson and Furter (*3*).

$$\log (\alpha_s/\alpha) = KN_3 \tag{2}$$

where $K = -0.384$ (Figure 6).

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NOMENCLATURE

D = percentage deviation in Herington's method
J = function of boiling points in Herington's method
K = constant in Equation 2
N_{s1} = solvation number of methanol relative to salt
N_3 = mole per cent of salt in three-component system
x = mole fraction of component in liquid phase
y = mole fraction of component in vapor phase
α = volatility of methanol relative to ethyl acetate
γ = liquid phase activity coefficient

Above nomenclature dimensionless

Subscripts

1 = methanol
2 = ethyl acetate
3 = calcium chloride
a = active
s = with salt
$'$ = salt-free basis

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