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Effect of Sodium Nitrate on the Vapor–Liquid Equilibria of the Methanol–Water System

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The effect of sodium nitrate on the vapor–liquid equilibria of the methanol–water system has been investigated under the atmospheric conditions of 760 ± 3 mmHg pressure by using a Smith and Bonner type of equilibrium still. Experiments were carried out at various concentrations of salt. The addition of increased amounts of salt enhanced the relative volatility of methanol and seemed to decrease the activity coefficients of the components of the system. The results obtained are indicative of the possible hydration and hydrotropism of ions for the methanol–water system. The improvement factor (i.e., the ratio of relative volatilities with and without salt present) could be correlated semiempirically as a function of salt concentration in the manner suggested by Johnson and Furter, showing a linear dependence of the salt effect on the salt concentration of the liquid.

An important technique in extractive distillation is the use of inorganic salt as extractive agent to modify the relative volatility of the binary mixture. As the addition of salt to a binary solution has a notable effect on the vapor–liquid equilibrium of the system, it has been the normal tendency for investigators to conduct these studies under saturated conditions of the salt though the addition of relatively small amounts of salts may serve the purpose in either shifting appreciably or breaking the azeotrope in the case of binary azeotropic systems or in enhancing the relative volatility of the desired component in the case of nonazeotropic systems comprising components exhibiting almost the same volatilities. It would also be desirable to ascertain in such studies how the improvement factor varies with varying concentrations of the salt in question. A few investigations reported (*1*, *5*, *9*, *11*, *13*, *17*) about the effect of the addition of salts of varying concentrations have also included correlation of salt effect with the salt concentration of the liquid. Both methods of correlation, the "improvement factor" method and the "special binary" method have been dealt with in detail by Furter (*2*, *3*). The results from a similar study of the effect of sodium nitrate on the vapor–liquid equilibrium relationships of methanol–water systems are described in this presentation.

Experimental Section

The vapor–liquid equilibrium data were determined by using a Smith and Bonner type of still with an arrangement for magnetic stirring. The description and working of the still have been detailed elsewhere (*15*, *16*). The experimental technique and procedure were the same as described in earlier papers (*12*, *13*) except for the modification in the liquid composition estimation method. The liquid sample at the end of each run was analyzed for its methanol content on a salt-free basis by first separating it quantitatively into salt and methanol–water fractions by a total distillation technique of evaporation to dryness and then analyzing for the alcohol–water ratio. The vapor samples were analyzed directly by the specific gravity–composition method with the specific gravities determined at 30 ± 0.05 °C. The vapor–liquid equilibrium data for the methanol–water system were obtained at three concentrations of sodium nitrate salt, the concentrations being 0.05, 0.07, and 0.08 mole fraction of salt in the ternary mixture. The salt concentrations in the liquid were established by adding known weights of dried salt to known quantities and compositions of alcohol–water mixtures previously prepared. The equilibrium data were determined at atmospheric pressure which remained constant in the range 760 ± 3 mmHg. The methanol and sodium nitrate used were BDH AnalaR reagent grade and the water was laboratory distilled.

The performance of the equilibrium still for the determination of data in the presence of dissolved salts was earlier assessed by measuring data for the system cyclohexane–carbon tetrachloride–ammonium sulfate, the salt being present under saturated condition. The vapor–liquid equilibrium data obtained compared well with the reported data (*13*) for this system.

Results

The experimental results on the vapor–liquid equilibrium of methanol–water at three concentrations of sodium nitrate, viz., 0.05, 0.07, and 0.08 mole fraction, are presented on a salt-free basis in Table I and plotted as an x–y diagram in Figure 1. The binary data (i.e., without sodium nitrate present) reported in ref 4 and those of Johnson and Furter (*8*) under saturated sodium nitrate have also been included in the figure for comparison purpose. To study the effect of salt, we computed the improvement factor which is the ratio of relative volatilities with and without salt present for varying concentrations of the salt at various fixed values of x_1, the methanol mole fraction employing the data in the presence of salt obtained in this investigation and the reported binary data (*4*) in the absence of salt. The values of $\ln(\alpha_S/\alpha)$ thus calculated and presented in Table II are also plotted against salt concentrations for the various

Table I. Vapor-Liquid Equilibrium and Activity Coefficient Data for the Methanol (1)-Water (2)-Sodium Nitrate System

x_1	y_1	t, °C	activity coeff γ_1	activity coeff γ_2
(a) Concentration of Sodium Nitrate, 0.05 mole fraction				
0.00	0.00	103.5		
0.035	0.214	92.2	2.1939	1.1208
0.122	0.521	86.2	2.0606	1.0520
0.175	0.607	83.7	1.8229	1.0226
0.224	0.665	81.5	1.6850	1.0807
0.460	0.825	74.2	1.3220	1.005
1.000	1.000	66.1		
(b) Concentration of Sodium Nitrate, 0.07 mole fraction				
0.00	0.00	106.4		
0.065	0.465	94.0	2.6664	0.8802
0.155	0.621	87.2	1.8661	0.6603
0.221	0.691	83.5	1.6599	0.634
0.341	0.774	79.2	1.6828	0.5429
1.000	1.000	66.1		
(c) Concentration of Sodium Nitrate, 0.08 mole fraction				
0.00	0.00	107.2		
0.07	0.51	95.1	2.6205	0.7898
0.161	0.661	87.5	1.8956	0.8081
0.231	0.722	84.9	1.5940	1.030
1.000	1.000	66.1		

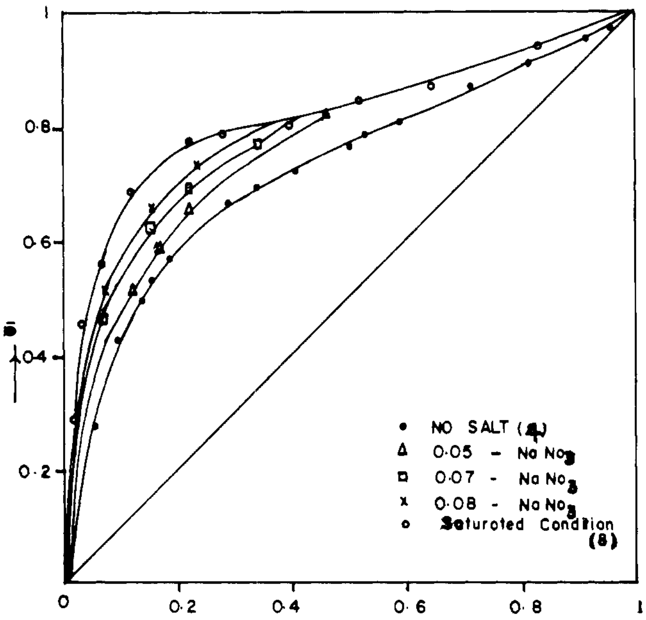

Figure 1. Plot of x_1 vs. y_1 for the system methanol (1)-water (2)-sodium nitrate: (●) no salt (*4*); (Δ) 0.05 mole fraction $NaNO_3$; (□) 0.07 mole fraction $NaNO_3$; (×) 0.08 mole fraction $NaNO_3$; (O) saturated condition (*8*).

fixed values of x_1 in Figure 2. These plots turned out to be straight lines indicating the simple linear dependence of the salt effect on the salt concentration of the liquid, that is (*7*)

$$\ln (\alpha_S/\alpha) = kZ$$

where α_S is the relative volatility of methanol with respect to water in the presence of sodium nitrate, α is the relative volatility in the absence of salt, Z is the mole fraction of salt in the methanol-water-sodium nitrate mixture, and k is the proportionality factor.

The proportionality factor k has been observed to decrease slightly with an increase in the x_1 value in the concentration region studied. The liquid-phase activity coefficient was calculated for the experimentally determined equilibrium compositions by applying the correction for saturation vapor pressure of components in the presence of salt, that is, by treating the ternary system as a pseudobinary and accounting for vapor pressure depression due to the presence of salt as suggested by Furter et al. (*6*). The relationship used is

Table II. Variation of Improvement Factor with Salt Concentration of the Liquid for the Methanol (1)-Water (2)-Sodium Nitrate System

x_1	Z (salt concn), mole fraction	y_1	α	α_S	log (α_S/α)
0.10	0.0[b]	0.45[a]			
	0.05	0.475		8.143	0.0436
	0.07	0.540	7.364	10.565	0.1567
	0.08	0.570		11.93	0.2095
	satd[c]	0.645[a]		16.352	0.3464
0.15	0.0[b]	0.535[a]			
	0.05	0.565		7.308	0.0496
	0.07	0.615	6.519	9.079	0.1425
	0.08	0.640		10.07	0.189
	satd[c]	0.715[a]		14.216	0.3385
0.20	0.0[b]	0.605[a]			
	0.05	0.630		6.811	0.0461
	0.07	0.670	6.126	8.121	0.1225
	0.08	0.695		9.114	0.1896
	satd[c]	0.750[a]		12.0	0.2920
0.25	0.0[b]	0.655[a]			
	0.05	0.688		6.375	0.0489
	0.07	0.715	5.696	7.5263	0.121
	0.08	0.740		8.853	0.1752
	satd[c]	0.775[a]		11.711	0.313
0.30	0.0[b]	0.690[a]			
	0.05	0.720		6.00	0.0627
	0.07	0.750	5.193	7.01	0.1296
	0.08	0.775		8.037	0.1896
	satd[c]	0.795[a]		8.628	0.2204

[a] Literature values (*4*, *8*). [b] No salt. [c] Saturated condition.

Table III. Correction Factors in Methanol (1)-Water (2)-Sodium Nitrate

salt concn (mole fraction)	ϵ_1	ϵ_2
0.05	0.9489	0.8694
0.06	0.9489	0.8103
0.08	0.9489	0.7983

$$\gamma_i = y_i P / x_i p_i'$$

where x and y are on a salt-free basis and p_i' is the corrected vapor pressure given by $p_i' = p_i^0 \epsilon_i$ in which p_i^0 is the saturation vapor pressure in the absence of salts at system temperature and ϵ_i the correction factor. The correction factors for the two components as computed by the method followed by Furter et al. (*6*) are listed in Table III for the three salt concentrations studied.

The vapor pressure values at desired temperatures were obtained by using the Antoine equation with the constants in the equation taken from literature (*10*). The activity coefficient thus computed using the experimental y-x data and assuming ideal behavior of the mixture in the vapor phase are presented in Table I.

It may be concluded that even though a definite trend in the activity coefficient values of the water component in this concentration range could not be observed in the present set of data, a reduction in magnitude at higher concentrations of salt is indicative of possible strong interaction between sodium nitrate and water in the form of hydration of ions resulting in a "salting out" effect due to the attraction between water molecules and ions which in turn results in the reduction of activity of water. The possibility of hydrotropism which may entail the "salting in" effect (that is, lowering the relative volatility between the com-

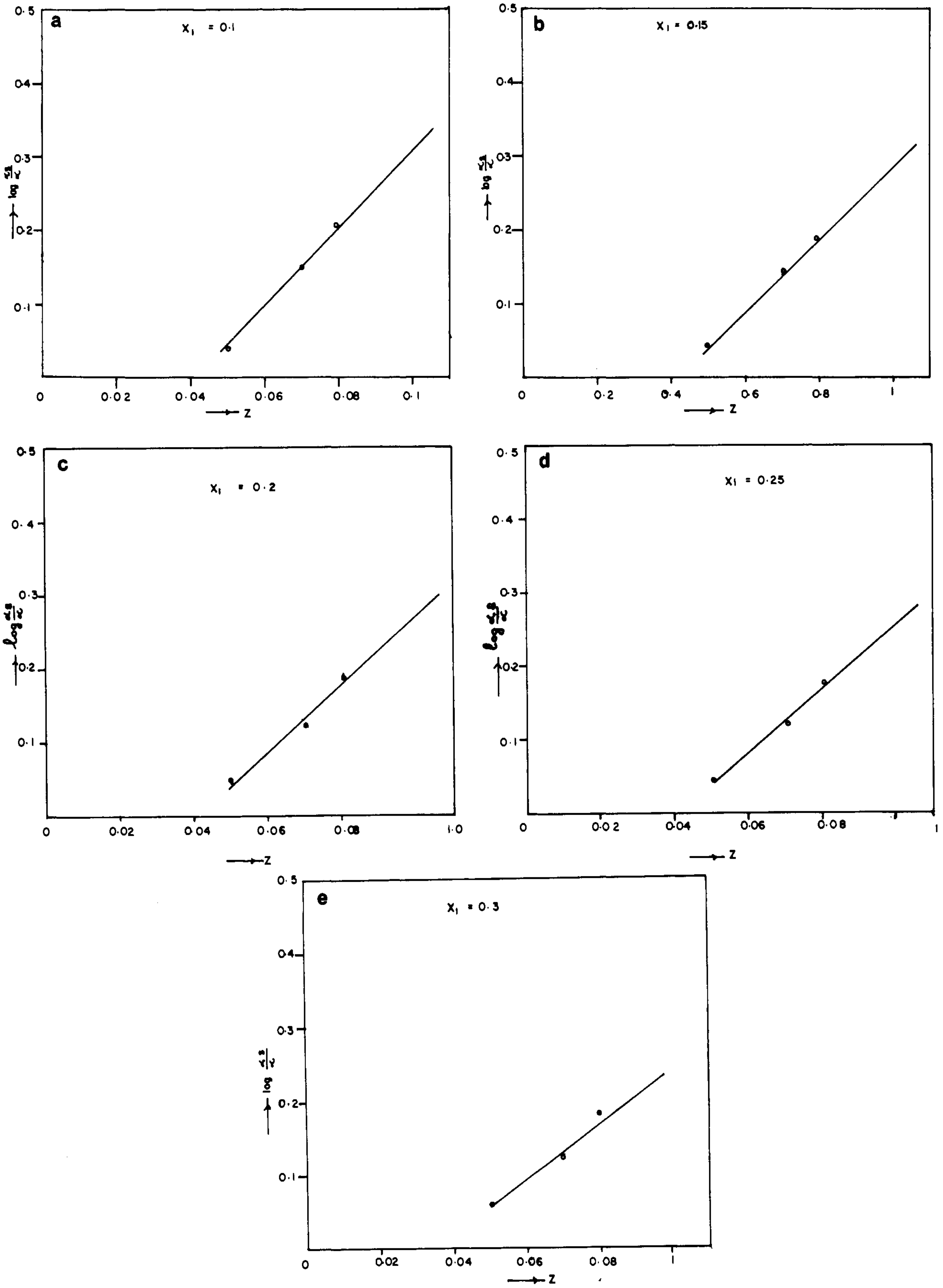

Figure 2. Plot of Z vs. log (α_S/α) for the system methanol (1)-water (2)-sodium nitrate: (a) for x_1 = 0.10; (b) for x_1 = 0.15; (c) for x_1 = 0.20; (d) for x_1 = 0.25; (e) for x_1 = 0.30.

ponents of the system) and which happens by the congregation of methanol molecules around one of added ions might not be high in this system in view of the very low solubility of sodium nitrate in the methanol component.

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Glossary

P	system pressure, mmHg
p_i^0	saturation vapor pressure of component i in the absence of salt, mmHg
p_i'	corrected vapor pressure of component i, mmHg
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 on a salt-free basis
Z	mole fraction of salt in the liquid phase = (mole of salt)/(mole of alcohol + mole of water + mole of salt)

Greek Letters

α	relative volatility of methanol with respect to water in the absence of the salt sodium nitrate
α_S	relative volatility with the salt present, calculated by using the liquid composition on a salt-free basis
γ_i	activity coefficient in the liquid phase of component i
ϵ_i	correction factor for the computation of the activity coefficient given by P/p_i'' where p_i'' is the vapor pressure of pure component i at the temperature at which component i boils in the presence of salt under the respective concentration of salt

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Thermodynamics of Nucleoside–Solvent Interactions: Inosine and Adenosine in Water and in 1 *m* Ethanol between 25 and 35 °C

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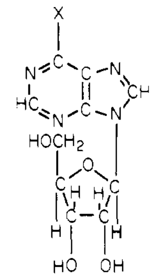
Enthalpies of solution of inosine and adenosine in water and in 1 *m* ethanol were measured at 25, 30, and 35 °C. Both nucleosides differ only by the functional groups OH and NH_2 and have approximately equal enthalpies of transfer from water to aqueous ethanol (0.48 and 0.47 kcal/mol at 25 °C for inosine and adenosine, respectively). The magnitude of the enthalpy of transfer is compared with those for the related purines caffeine and theophylline in the same solvent systems. Heat capacities of solution were obtained from the temperature variation of the enthalpies of solution (29 and 27 cal/(mol K) in water 38 and 18 cal/(mol K) in 1 *m* ethanol for inosine and adenosine, respectively). These values were combined with estimated heat capacities of the solids to yield partial molar heat capacities (96 and 95 cal/(mol K) in water for inosine and adenosine, respectively), showing that solute–solvent interaction in water is insensitive to the interchange of OH and NH_2. Heat capacities of transfer of each nucleoside from water to the mixed solvent indicate that the presence of ethanol tends to minimize the leveling effect induced by water on these functional groups. Estimated temperature coefficients of solubility of the nucleosides were calculated from the enthalpies and heat capacities of solution.

Introduction

This contribution reports on the enthalpies and heat capacities of solution of inosine and adenosine in water and in 1 *m* ethanol at 25, 30, and 35 °C. The two nucleosides were chosen for the following reasons: Inosine and adenosine are important components of ribonucleic acids, differing only in the functional groups OH and NH_2. They are derivatives of purines which include the previously studied caffeine and theophylline (*1–3*). Both nucleosides are sufficiently soluble for calorimetric measurements (*4*) and contain both polar and apolar groups whose interaction with water is important to the conformational stability of nucleic acids (*5*). Ethanol was chosen as a cosolvent because of its well-known but poorly understood effect in altering the solvent properties of water (*6*).



X = OH, inosine
X = NH_2, adenosine

Before the behavior of large complicated biochemical molecules in aqueous solutions can be understood, the data of interaction of their component parts in such systems must be determined.

Enthalpies of transfer were obtained from the difference in enthalpies of solution: $\Delta\bar{H} = \Delta H - \Delta H^\circ$. Values of ΔC_p were

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