exhibits positive deviations from Raoult's law while the system chlorobenzene-*p*-xylene exhibits negative deviations from Raoult's law.

Glossary

B_{11}, B_{22}	gas-phase second virial coefficient for component 1 and 2, respectively
P	total pressure, mmHg
p_1°	vapor pressure of component 1, mmHg
R	universal gas constant, 82.054 cm^3 atm K^{-1} mol^{-1}
T	absolute temperature, K
V_1^L	liquid molar volume of component 1, cm^3/mol
x_1, x_2	mole fraction of components 1 and 2, respectively, in liquid phase
y_1	mole fraction of component 1 in vapor phase
γ_1	activity coefficient of component 1.
δ_{12}'	$B_{12} - B_{11} - B_{22}$ where B_{12} is the second virial cross coefficient
λ_{12}, λ_{21}	constants in Wilson's equation

Subscripts

1	low boiling component
2	high boiling component

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Salt Effect on the Vapor Pressure of Pure Solvents: Methanol with Seven Salts at 24.9 °C

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Vapor pressure data of methanol at 24.9 °C with seven salts (LiCl, NaBr, $CaCl_2$, NaOH, NaI, KI, and $CuCl_2$) are presented. Attempts to correlate the results to crystallographic radii, or salt solubility in methanol, were inconclusive. For the two salts with I^- as common ion (NaI and KI), increased ΔP values follow decreasing values at the cation radii. This is not the case for the three salts with Na^+ as common ion (NaOH, NaI, NaBr) or for the two salts with Cl^- as common anion (LiCl, $CuCl_2$, $CaCl_2$). Considering salt solubility for the three salts with Na^+ as the common ion, vapor pressure depression effects increase with increasing salt solubility. The same was true for the two salts with I^- as common ion but not for the three salts with Cl^- as common ion (LiCl, $CuCl_2$, $CaCl_2$).

Introduction

While data for the vapor pressure depression of a large number of salts in water are available, see for example Weast (*13*), such data for nonaqueous solvents are rather scarce. Data for methanol with seven salts at 24.9 °C are presented in this paper. This represents part of a more general effort for the development and correlation of data for solvent-salt systems (Bekerman and Tassios (*2*)).

Experimental Section

An experimental study was conducted to determine the concentration effect of seven salts on the vapor pressure of methanol at 24.9 °C. Solutions of varying concentrations were charged to an Othmer still (*7*, *8*). The still was continuously heated while the pressure was adjusted until the liquid solution was boiling at a temperature of 24.9 ± 0.1 °C. When the temperature remained constant for about 30 min, the system was assumed to be in equilibrium and the pressure was measured using a cathetometer and a mercury manometer. The pressure was recorded as the vapor pressure of the system. The pressure in the still was controlled to within ±0.1 mmHg by a control system featuring a Precision Micro Set Manostat (*1*). The temperature was measured with a calibrated mercury-in-glass thermometer immersed in the liquid phase. The pressure in the still was measured with mercury manometer with the use of a cathetometer. Experimental details are given by Bixon (*3*).

Reagents and Chemicals

1. "Baker Analyzed" reagent grade sodium hydrozide was used for the sodium hydroxide runs. The assay was 98.3% NaOH. The largest impurity present was sodium carbonate listed as 0.4%. Before each run, an unknown impurity was filtered out from the NaOH—methanol solution with coarse grade filter paper. The impurity was probably the sodium carbonate since it is insoluble in methanol (*13*). The other impurities were not listed on the label.

2. Two different types of lithium chloride were used in these experiments. The first brand used was from Fisher Scientific Co. while the other brand was "Baker Analyzed" reagent grade. Both grades were listed as being 99.8% pure.

3. The cupric chloride was certified anhydrous grade from Fisher Scientific. The impurities listed on the label totaled 0.06%.

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Table I. Pressure-Composition Data: Methanol-LiCl

molality, mol kg^{-1}	pressure, mmHg	molality, mol kg^{-1}	pressure, mmHg
0.8096	118.8	3.1868	93.4
1.2880	114.6	3.8630	81.7
1.9132	106.0	4.3791	68.3
2.3994	100.0	5.3554	59.3
2.5768	99.9		

Table II. Pressure-Composition Data: Methanol-NaBr

molality, mol kg^{-1}	pressure, mmHg	molality, mol kg^{-1}	pressure, mmHg
0.560	123.4	1.215	117.9
0.753	121.7	1.274	117.6
0.882	121.1	1.389	116.7
0.891	120.8	1.556	114.8
1.180	118.0		

Table III. Pressure-Composition Data: Methanol-$CaCl_2$

molality, mol kg^{-1}	pressure, mmHg	molality, mol kg^{-1}	pressure, mmHg
0.3186	121.7	1.8799	103.0
0.8831	116.6	2.4254	94.1
1.2405	111.8	2.6345	89.6
1.3944	111.4		

Table IV. Pressure-Composition Data: Methanol-NaOH

molality, mol kg^{-1}	pressure, mmHg	molality, mol kg^{-1}	pressure, mmHg
0.3400	120.8	3.1721	81.5
0.8504	114.2	4.1500	67.7
1.1232	110.6	4.9077	58.6
2.2787	95.1	5.9413	48.6
2.7113	87.0		

Table V. Pressure-Composition Data: Methanol-NaI

molality, mol kg^{-1}	pressure, mmHg	molality, mol kg^{-1}	pressure, mmHg
0.2308	123.3	1.7031	106.9
0.3659	122.5	2.1796	102.5
0.6767	119.3	2.3222	101.5
0.7601	119.4	2.4523	98.0
0.7837	119.0	2.7593	95.5
1.1256	113.2	2.7648	95.1
1.3870	112.1	3.2387	89.0
1.6237	109.7	4.5200	72.8

4. The calcium chloride used was "Baker Analyzed" reagent grade and was listed at 98.4% purity.
5. The sodium iodide used was Mallinckrodt granular analytical reagent. The impurities listed on the label totaled 0.055%.
6. The sodium bromide used was Mallinckrodt analytical reagent with 99.0% minimum purity.
7. The potassium iodide used was "Baker Analyzed" reagent with 99.5% minimum purity.
8. The silver nitrate, used for titrations, was Certified ACS crystal from Fisher Scientific. Its purity was listed as being 99.9%.
9. The hydrochloric acid, used also for titration, was certified as 0.1000 N by Harleco Chemicals.

Table VI. Pressure-Composition Data: Methanol-KI

molality, mol kg^{-1}	pressure, mmHg	molality, mol kg^{-1}	pressure, mmHg
0.3680	124.3	0.6996	122.1
0.4718	124.1	0.7912	121.6
0.4919	123.8	0.9635	120.8
0.5788	123.3	1.1219	119.5
0.6525	122.5		

Table VII. Pressure-Composition Data: Methanol-$CuCl_2$

molality, mol kg^{-1}	pressure, mmHg	molality, mol kg^{-1}	pressure, mmHg
0.3868	122.6	2.3047	112.5
0.7294	120.7	2.4751	111.7
1.0334	119.0	2.7342	108.2
1.0928	120.2	3.3957	102.9
1.6263	115.7	3.8700	100.3
1.6755	116.6	3.9739	97.8
2.1463	113.0		

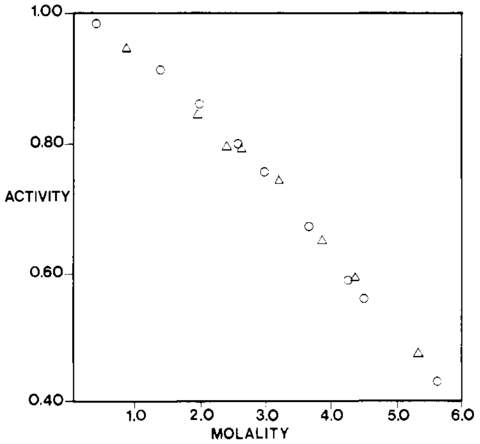

Figure 1. Variation of activity with molality for the system methanol-lithium chloride: ○, Skabichievski (*11*); △, this study.

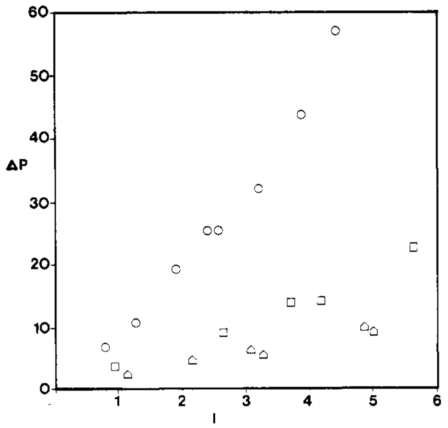

Figure 2. Vapor pressure depression for three salts with Cl^- as common ion at 24.88 °C: ○, lithium chloride; □, calcium chloride; ⌂, copper chloride.

10. Two different brands of methanol were used. The first brand was from Fisher Scientific Co. and was certified as being 99.9 mol % pure. The second type used was "Baker Analyzed" reagent and was listed as being 99.8% minimum purity. The average value of the vapor pressure at 24.9 °C was 125.5 mmHg which compares well with the value of 126.1 reported by Dever et al. (*4*).
11. The indicators used were standard solutions of 1 M potassium chromate for the Mohr titrations and standard methyl

red indicator for the sodium hydroxide determinations.

Results and Discussion

Tables I through VII present total pressure data as a function of the salt concentration for the seven salts studied. For comparison purposes Figure 1 presents a plot of the activity value

$$a = P/P^s \qquad (1)$$

(P is total pressure, P^s is vapor pressure of solvent) vs. molality for the system LiCl–methanol along with the data of Skabichievski (*11*) at 25 °C. The agreement between the two sets of data is satisfactory.

An examination of the vapor pressure depression

$$\Delta P = P^s - P \qquad (2)$$

for the two salts with I^- as common ion (NaI, KI) indicates that increased ΔP values (NaI > KI) follow decreasing values of cation crystallographic radii ($Na^+ < K^+$). For the three salts with Na^+ as common ion (NaOH, NaI, NaBr), however, increased values of ΔP (NaOH > NaI > NaBr) do not correspond to decreasing values of anion radii ($OH^- < Br^- < I^-$). Finally, to establish the order of increasing ΔP values for the three salts with Cl^- as common ion (LiCl, $CuCl_2$, $CaCl_2$) consider Figure 2 where ΔP is plotted against the ionic strength, I

$$I = \tfrac{1}{2}\sum_{i}^{N} m_i z_i^2 \qquad (3)$$

where m_i = molality of ion i, z_i = charge of ion i, and N = number of ion types per molecule.

Use of I, instead of m, is made in this case to take into account the fact that LiCl is a 1–1 salt and $CuCl_2$ and $CaCl_2$ are 2–1 salts. The plots indicate that increasing ΔP effects (LiCl > $CaCl_2$ > $CuCl_2$) again do not follow decreasing ionic radii ($Li^+ < Cu^{2+} < Ca^{2+}$). Similar observations can be found in the literature. For example, while Tsiparis and Smorigaite (*12*) report that the salting-out effects of acetic acid in mixtures with water increases with decreasing ionic radius, the results of Sada et al. indicate that this is not the case for tetrahydrofuran–water mixtures (*9*) or for the solubility of toluene in aqueous salt solutions (*10*). Apparently, the ion solvation, which determines the P effect, cannot be related in a simple fashion to the ionic crystallographic radii (*6*).

An attempt to correlate vapor pressure depression effects to salt solubilities in methanol (*5*) provided also inconclusive. For the three salts with Na^+ as common ion, and the two with I^-, increased ΔP effects correspond to increased salt solubilities. However, this was not the case for the three salts with Cl^- as common ion.

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Solubility of Carbon Dioxide in Aqueous Electrolyte Solutions

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The solubility of CO_2 in aqueous solutions of 16 electrolytes has been determined by the gas volumetric method at 1 atm and temperatures of 15, 25, and 35 °C. The maximum concentration of each aqueous electrolyte solution was above 60 wt % of saturation. For the solubility of CO_2 over the wide ranges of electrolyte concentration, it was found that the empirical Setschenow equation was not applicable to some systems. The data of those systems were correlated by a two-parameter equation within a deviation of 2%.

The solubility of carbon dioxide in aqueous electrolyte solutions has been investigated by many workers. However, there have been few data which were measured over wide ranges of electrolyte concentration with a sufficient number of points to investigate the effect of electrolyte concentration on the solubility of gas for each solution.

The empirical Setschenow equation has often been used to correlate between the activity coefficient of the nonelectrolyte solute and the concentration of the electrolyte up to the moderate concentrations and has in many cases given sufficient results for correlation, though this equation is a first approximation valid at low electrolyte concentrations. As was shown by Markham and Kobe (*6*) and Clever and Reddy (*2*), however, the equation was not valid in some systems. Markham and Kobe (*6*) proposed a two-parameter equation to fit the data of these systems.

The method of van Krevelen and Hoftijzer (*11*) based on the empirical Setschenow equation has widely been used to estimate the solubilities of gases in electrolyte solutions. The estimated results by this method are often poor, however.

In this experiment, solubilities of carbon dioxide in a number of aqueous electrolyte solutions over wide ranges of concentration were determined to inspect the applicabilities of the correlating and estimating methods.

The electrolytes used were NaCl, $NaNO_3$, KCl, KNO_3, NH_4Cl, $(NH_4)_2SO_4$, Na_2SO_4, K_2SO_4, $MgCl_2$, $Mg(NO_3)_2$, $MgSO_4$, $CaCl_2$, $Ca(NO_3)_2$, $BaCl_2$, $AlCl_3$, and $Al_2(SO_4)_3$.

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