Research Journal of Pharmaceutical, Biological and Chemical Sciences

Prediction of salting coefficient for Acetone-Methanol-Salt System using Scaled Particle Theory.

J Dhanalakshmi*, B Deepak Kumar, S Aravind, S Ayyappan, and B Ambedkar

Department of Chemical Engineering, SSN College of Engineering, Kalavakkam, Chennai 603 110, TN, India

ABSTRACT

The prediction of salting coefficient for acetone-methanol system is important to identify a suitable salt in order to break the azeotropic composition. Scaled particle theory has been used for the separation of acetone-methanol system by screening of salts. The scaled particle theory is a purely qualitative theoretical approach to estimate the salt effect on acetone-methanol system. In the present study, the salt effect on acetone-methanol system containing inorganic salts has been examined and the results are discussed. Further, the influence of ions of the salt is also discussed. The predicted salting coefficient is validated with literature experimental data.

Keywords: acetone, methanol, scaled particle theory, salting coefficient, salt effect

*Corresponding author
Email id: dhanalakshmij@ssn.edu.in

1. INTRODUCTION

The azeotrope of an acetone-methanol mixture is 79 mole% of acetone at azeotropic temperature 328.25 K and it cannot be further concentrated by ordinary distillation. In organic synthesis, acetone of higher concentration is required. Using salt in extractive distillation process, a 98-99 mole% acetone can be produced [1, 2]. Hence, phase equilibrium studies of acetone-methanol-salt system are highly essential. Analysis of literature shows that most of the work performed for non-polar systems to estimate their salt effect in binary azeotropic mixtures whereas the theoretical prediction of salt effect on the polar systems has received only minor attention.

The different salts produce salting out or salting in effect on the azeotropic mixtures. The various techniques for the estimation of salt effect namely electrostatic & hydration theory of salt in solution, effect of internal pressure and Vander Waals force for solvation of salt. The above theories dependent on experimental data or cannot be applied for a wide range of concentrations. Except, scaled particle theory, is derived based on statistical thermodynamics and physics, independent of experimental data to evaluate salt effect using known molecular parameters [3-5]. Hence, the scaled particle theory is promising method to estimate the salt effect on polar systems. The objective of the present study is the application of scaled particle theory to estimate the salting coefficients in a ternary system of acetone-methanol-salt system.

2. Scaled Particle Theory

The salt effect on acetone (1) - methanol (2) - salt (3) system can be studied by qualitative approach namely scaled particle theory. The solubility of an electrolyte (acetone) in non-aqueous solution at lesser salt concentration is given below [6],

$$\log S_o/S = k_s c \tag{2.1}$$

where S_o refers to solubility of component 1 in pure component 2 (methanol), S refers to solubility of component 1 in non-aqueous salt solution containing component 2, c is the salt concentration in non-aqueous solution and k_s is the salting coefficient. If k_s is positive, salting out ($S_o > S$) and salting in is observed ($S_o < S$) for negative k_s.

2.1 Estimation of Salting Coefficient

The salt which when dissolved in the azeotropic solution, dissociated into ions. At lower salt concentrations, the solubility of salt in the binary azeotropic mixture can be calculated by using Setschenow equation (2.1).

$$k_s = -(\frac{d(\log S)}{d(c)})_{c \to 0} \tag{2.1.1}$$

Shoor and Gubbins [7] derived the expression to calculate the salting coefficient for polar systems by considering various molecular interactions in solution such as ion-ion, ion-dipole and dipole-dipole interactions and it is given as

$$-\log S = \frac{\overline{g_1^h}}{2.3kT} + \frac{\overline{g_1^s}}{2.3kT} + \log kT \sum_{j=1}^{4} \rho_j \tag{2.1.2}$$

where g_1^h is the free energy change for cavity formation in the solution, g_1^s is the change in free energy to introduce nonelectrolyte molecule into the cavity and ρ_j is the number density (particles/cc) of components in a solution. Subscripts 1, 2, 3 and 4 are used to denote acetone, methanol, cation and anion of the salt respectively.

Combining equations (2.1.1) and (2.1.2)

$$k_s = \left[\frac{d(\overline{g_1^h}/2.3kT)}{d(c)} \right]_{c \to 0} + \left[\frac{d(\overline{g_1^s}/2.3kT)}{d(c)} \right]_{c \to 0} + \left[\frac{d(\log \sum \rho_j)}{d(c)} \right]_{c \to 0}$$

(2.1.3)

$$k_s = k_\alpha + k_\beta + k_\gamma$$

(2.1.4)

where, k_α, k_β, k_γ represent their incorporation to salting coefficient individually. In this study, the application of scaled particle theory to polar molecule (acetone) in non-aqueous system is derived to estimate the salting coefficient for 1:1 and 1:2 electrolytes. The expression for k_α, k_β, k_γ is given (Appendix) using available physico-chemical parameters of ions and polar molecules. The required molecular parameters to calculate the salt effect namely are infinite molal volume (ϕ_o) of the salt, diameters (σ) and polarizabilities (α) of ions and molecule.

3. RESULTS AND DISCUSSION

The molecular parameters required to obtain salting coefficient is given in Table 1 to 3. The relative contributions of k_α, k_β, and k_γ are also given in Table 4 and 5 for univalent and bivalent salts respectively. It is observed that the magnitude of k_γ is seems to be a smaller one when compared to k_α and k_β. Taking the uncertainties in k_α and k_β, the contribution from k_γ can be neglected. It is evident that k_α remains positive since cavity formation due to free energy change tends to positive for increasing salt concentration in the solution. In this sense, it is not possible to build the cavity shape in the salt solution rather in pure methanol. k_β values are negative. The negative sign indicates that it is much easier to accommodate the electrolyte molecule in a cavity of salt solution when compared to pure solvent (methanol). The sign of k_s will depend on the relative magnitudes of k_α and k_β [8, 9]. It is shown that the k_β, has much more influence on the overall salting coefficient than k_α. It closely adheres to the pattern of increasing size of the anion exhibits greater salting coefficients.

Table 1. Physical properties of polar molecules[1]

Molecule	σ (˚A)	α 10^{-24} (cc)	ε/κ (K)
Acetone	4.40	2.85	424
Methanol	3.71	3.27	385

[1]From Treiner[13] .

Table 2. Ionic parameters required for scaled particle theory[1]

[1]From Xu and Hu [14].

Ion		σ(˚A)	α 10^{-24} (cc)	Z_j
Cation	Na$^+$	1.90	0.210	10
	K$^+$	2.66	0.870	18
	Ca^{2+}	1.98	0.510	18
	Zn^{2+}	1.48	0.112	28
Anion	Cl$^-$	3.62	3.020	18
	SCN$^-$	2.56	3.03	28
	NO$_3^-$	4.05	4.365	30

Table 3. Apparent molal volumes of bivalent salt in methanol at infinite dilution[1]

Salt	$\Phi_o \times 10^6$ (m³/mol)[1]
$Zn(NO_3)_2$	12.70
$ZnCl_2$	7.50
$Ca(NO_3)_2$	8.53
$CaCl_2$	11.20

[1]From Marcus and Hefter [15]

3.1 Effect of Cations

It is found that all the monovalent and bivalent salts of the nitrates gives higher salting coefficient (Table. 4 & 5) and this exhibits elimination of azeotrope in the binary system. The order of increasing salting coefficient is Calcium nitrate > Zinc nitrate > Calcium chloride > Zinc chloride > Sodium nitrate > Potassium nitrate and thiocyanate. In the above, the reverse trend found in their apparent molal volume and polarizability of various cations considered. The decreasing salting coefficient is observed for increasing size and the polarizabilities of cation. It may be because cation posses the charge and the quantity of ions generates in non-aqueous solution. The similar behaviour has already described for aqueous system in the literature [10, 11]. In addition, the interaction between ion-solvent pair for both monovalent cation and bivalent cation inorganic salts are determined by taking account of dipole-ion and dipole-dipole molecular interactions in k_β terms. This leads to estimate the salting coefficient including k_α and k_β. It is obvious that as stated in the electrostatic theory, the size of cation decreases it attracts more dipole molecules towards it and thus increasing salting coefficient results in higher salt effect in azeotropic systems aid for better separation. This is concurred with the experimental and scaled particle theory results. The both results showed that higher salting coefficient is obtained for monovalent salts ($Na^+ > K^+$) and bivalent salt ($Zn^{2+} > Ca^{2+}$) respectively.

Table 4. Salting coefficients of univalent for acetone-methanol system using scaled particle theory at 25 ˚C

Ion	Salt	k_α	k_β	k_γ	k_s
NO_3^-	$Ca(NO_3)_2$	5.083	-0.0831	0.0488	4.9369
	$Zn(NO_3)_2$	4.844	-.01173	0.0469	4.7321
Cl^-	$CaCl_2$	4.273	-0.0303	0.0783	4.3215
	$ZnCl_2$	3.289	-0.0630	0.0442	3.2711

Table 5. Salting coefficients of bivalent for acetone-methanol system using scaled particle theory at 25 ˚C

Ion	Salt	k_α	k_β	k_γ	k_s
NO_3^-	$NaNO_3$	2.404	-0.245	0.0342	2.417
	KNO_3	2.274	-0.292	0.027	2.091
Cl^-	$NaCl$	2.503	-0.264	0.015	2.254
	KCl	2.046	-0.052	0.035	2.025
SCN^-	$NaSCN$	2.297	-0.209	0.026	2.114
	$KSCN$	1.984	-0.011	0.022	1.995

3.2 Effect of Anions

The salting coefficient of potassium thiocyanate, calculated using scaled particle theory exhibits similar trend of salting out effect as described earlier by Illiuta *et al.* [12]. In case of monovalent salt, the sodium and potassium nitrate has higher salting coefficient (Table 4). For bivalent salts, all the inorganic salts have higher salting coefficient when compared to univalent salts (Table 5). Larger salting out effect with a higher salting coefficient is obtained for the separation of azeotropic system. This is because of rise in molal volume of salts and polarizability of corresponding anions, which results as increase in salting coefficient. The polarizability of NO_3^- is greater so it attracts numerous of methanol molecule and therefore the NO_3^- ion interaction with methanol becomes stronger as the result. Thus, NO_3^- shows better salting effect as compared

to Cl⁻. This shows that anions with larger sizes, can give better salting out effect for the separation of acetone-methanol binary azeotropic system.

3.3 Calculation of Experimental Salting Coefficient

The Furter's equation for the calculation of salt effect on binary azeotropic system is given as

$$\ln(\alpha_s/\alpha_o) = Kz \qquad (3.1)$$

where K is salt effect of azeotropic system, z is salt concentration in the solution. This equation is applicable to a very low salt concentration and at constant liquid feed compositions. The experimental salting coefficient for the salts reported in literature, is estimated using the above equation and compared with scaled particle theory predictions, is given in Table 6. The deviation is high since the magnitude of chosen molecular parameters causes deviation in the salting coefficient, estimated from the scaled particle theory [13].

Table 6. Comparison of experimental and theoretical salting coefficients for acetone -methanol system at 25 ˚C

Salt	k_{exp}	k_{SPT}
KSCN	3.037	1.995
LiNO₃[1]	3.958	2.051

[1]From Vercher et al.[16].

APPENDIX : Derivation of Scaled Particle Theory to Acetone (1) - Methanol(2) – Salt(3) system

The theory illustrates the principle of extractive distillation to separate an azeotrope using salt as third component. The system under consideration consists of the following two solvents combined with salt, Acetone(1), Methanol (2). The subscripts 1, 2, 3 & 4 are used to represent acetone, methanol, cation of the salt and anion of the salt respectively.

For 1:1 electrolyte (monovalent salt),

Expression for k_γ:-

$$\rho_2 = \frac{Nd_2}{M_2}\left(1 - \frac{c\phi}{1000}\right), \quad \rho_3 = \rho_3 = \frac{Nc}{1000}$$

$$k_\gamma = 0.0351 - 4.34\times10^{-4}\phi$$

Expression for k_β:-

$$k_\beta = -1.85\times10^{14}\left(\frac{\varepsilon_1}{k}\right)^{\frac{1}{2}}\left[\alpha_3^{\frac{3}{4}}z_3^{\frac{1}{4}}\left(\frac{\sigma_1+\sigma_3}{\sigma_3}\right)^3 + \alpha_4^{\frac{3}{4}}z_4^{\frac{1}{4}}\left(\frac{\sigma_1+\sigma_4}{\sigma_4}\right)^3\right] + 3.011\times10^{16}\phi\left(\frac{\varepsilon_1}{k}\right)^{\frac{1}{2}}\left(\frac{\varepsilon_2}{k}\right)^{\frac{1}{2}}(\sigma_1+\sigma_2)^3 +$$

$$1.77\times10^{-2}\frac{\phi\alpha_1}{(\sigma_1+\sigma_2)^3}$$

Expression for k_α:-

$$k_\alpha = 4.01\times10^{20}\left(\sigma_3^3+\sigma_4^3\right) - 8.41\times10^{-4}\phi + \sigma_1\left[1.20\times10^{21}\left(\sigma_3^2+\sigma_4^2\right) + 5.29\times10^{28}\left(\sigma_3^3+\sigma_4^3\right) - 1.68\times10^5\phi\right]$$

$$+\sigma_1^2\left[1.20\times10^{21}\left(\sigma_3+\sigma_4\right) + 1.57\times10^{29}\left(\sigma_3^2+\sigma_4^2\right) + 8.17\times10^{36}\left(\sigma_3^3+\sigma_4^3\right) - 1.49\times10^{13}\phi\right]$$

For 1:2 electrolyte (bivalent salt),

Similarly, the above procedure is followed to obtain the salting coefficient for 1:2 electrolyte systems. The only difference is that the system considered here, is composed of two moles of cation and one mole of anion thereby leading to a change in density of the solution.

Expression for k_γ:-

$$\rho_2 = \frac{N d_2}{M_2}\left(1 - \frac{c\phi}{1000}\right), \quad \rho_3 = \frac{Nc}{1000}, \quad \rho_4 = \frac{2Nc}{1000}$$

$$k_\gamma = \frac{3M_2}{2300 d_2} - \frac{\phi}{2300}$$

Expression for k_β:-

$$k_\beta = -1.85\times10^{14}\left(\frac{\varepsilon_1}{k}\right)^{\frac{1}{2}}\left[\alpha_3^{\frac{3}{4}} z_3^{\frac{1}{4}}\left(\frac{\sigma_1+\sigma_3}{\sigma_3}\right)^3 + 2\alpha_4^{\frac{3}{4}} z_4^{\frac{1}{4}}\left(\frac{\sigma_1+\sigma_4}{\sigma_4}\right)^3\right] + 3.011\times10^{16}\phi\left(\frac{\varepsilon_1}{k}\right)^{\frac{1}{2}}\left(\frac{\varepsilon_2}{k}\right)^{\frac{1}{2}}\left(\sigma_1+\sigma_2\right)^3 +$$

$$1.77\times10^{-2}\frac{\phi\alpha_1}{\left(\sigma_1+\sigma_2\right)^3}$$

Expression for k_α:-

$$k_\alpha = 7.25\times10^{20}\left(\sigma_3^3+\sigma_4^3\right) - 8.41\times10^{-4}\phi + \sigma_1\left[8.41\times10^{20}\left(\sigma_3^2+\sigma_4^2\right) + 7.02\times10^{28}\left(\sigma_3^3+\sigma_4^3\right) - 1.68\times10^5\phi\right]$$

$$+\sigma_1^2\left[3.20\times10^{22}\left(\sigma_3+\sigma_4\right) + 4.57\times10^{30}\left(\sigma_3^2+\sigma_4^2\right) + 3.17\times10^{36}\left(\sigma_3^3+\sigma_4^3\right) - 1.49\times10^{13}\phi\right]$$

4. CONCLUSION

This study shows that the salt effect on acetone-methanol system can be performed by scaled particle theory. The salting coefficients obtained using scaled particle theory is in good agreement with the experimental results. Based on the scaled particle theory analysis, salt effect is due to anion compared to cation of the inorganic salt and also larger size of the anion gives better salting coefficients, hence anion based inorganic salts are more effective to break the azeotrope of acetone-methanol system.

5. REFERENCES

[1]   W.F.Furter, Salt Effect in Distillation: A Literature Review II, Can. J. Chem. Engg., **55** (1977) 229-239.
[2]   W. F. Furter, Extractive distillation by salt effect, Chem. Eng. Comm. 116 (1991) 35 - 40.
[3]   L. Wilcox, E. Schrier, Salt effects in alcohol-water solutions. An application of scaled particle theory to the salting out of polar molecules, J. Phys. Chem. **75** (1971) 24, 3757-3764.
[4]   Z. Lei, H. Wang, R. Zhou, Z. Duan, Influence of salt added to solvent on extractive distillation, Chem. Eng. J. **87** (1977) 49 - 156.
[5]   R.A. Pierotti, A scaled particle theory of aqueous and non-aqueous solutions, Chem. Rev. **76** (1976) 717-726.
[6]   W.L.Masterton, T.P.Lee, Salting coefficients from Scaled particle theory, J. Phys. Chem. **74** (1970) 1776-1782.
[7]   S.K.Shoor, K.E.Gubbins, Solubility of non-polar gases in concentrated electrolyte solutions -methanol system, J. Phys. Chem. **73** (1969) 498-505.
[8]   Z. Lei, R. Zhou, Z. Duan, Application of scaled particle theory in extractive distillation with salt, Fluid Phase Equilib., **200** (2002) 187-201.
[9]   R.Y.Sun, Molecular thermodynamics of salt effect in vapour-liquid equilibrium of ethanol-water systems, Fluid Phase Equilibria, **157**(1999) 29-40.
[10]   J. Dhanalakshmi, P.S.T. Sai, A.R. Balakrishnan, Effect of bivalent cation inorganic salts on isobaric vapor–liquid equilibrium of methyl acetate–methanol system. *Fluid phase Equilib*. **379** (2014) 114-118.

[11]   YF. Banat, S. Asheh, J. Simandl, Effect of trivalent, bivalent and univalent cation inorganic salts on the isothermal vapor-liquid equilibria of propionic acid - water system, Chem. Eng. Process. **42** (2003) 759-766.

[12]   M.C. Iliuta , F.C. Thyrion, and O.M. Landauer, Vapour – liquid equilibrium of acetone – methanol system in the presence of salt, **130 (**(1997) 253–269.

[13]   C. Treiner, Some regularities in the behaviour of salting constants for polar   molecules in aqueous electrolyte solutions, Can. J. Chem. **59** (1981) 2518-2526.

[14]   N.Xu, Y.Hu, Prediction of Henry's constants of gases in electrolyte solutions, *Fluid   Phase Equilib*, **30** (1986) 221-228.

[15]   Y. Marcus, G. Hefter, Standard partial molar volume of salt and ions in nonaqueous   solvents, Chem. Rev. **104** (2004) 3405-3452

[16]   [16]. E. Vercher, A.V. Orchillés, P. J. Miguel, V. González-Alfaro, Antoni Martínez- Andreu, Isobaric vapor-liquid equilibria for acetone-methanol-lithium nitrate at 100kPa. *Fluid phase Equilib* **250** (2006) 1,131-137