

Calculating the Critical Relative Humidity from the Solubility of Electrolyte According to Extended Non-random Two Liquid Model

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According to thermodynamic principle, the critical relative humidity of electrolytes is closely related to their solubility. The authors explored the relationship theoretically and calculated the critical relative humidity of 21 electrolytes in the light of Raoult's law, modified Debye–Hückel model and extended non-random two liquid (NRTL) model from their solubility. The results indicate that the critical relative humidity values calculated by Raoult's law can not accord with the reported ones and there is a systematic error in high concentration range; the values calculated by modified Debye–Hückel model still can not accord with the reported ones well although without systematic error; and the values calculated by extended NRTL are comparable to the reported ones.

Key words critical relative humidity; solubility; extended non-random two liquid model; modified Debye–Hückel model; Raoult's law

The critical relative humidity (*CRH*) and the solubility in water of electrolytes are important physical properties that affect the quality of foodstuff, drug, fertilizer, chemical and so on.^{1–4} However, the critical relative humidity is unclearly defined and there is little theoretical study reported. For example, there are two definitions of *CRH* in pharmaceuticals: 1) A water-dissoluble drug powder is sensitive to the humidity of surrounding air, above certain relative humidity, it will adsorb water. The critical relative humidity is defined as the relative humidity of atmosphere above which the drug powder starts to rapidly adsorb water at a given temperature.⁵ 2) There is equilibrium between gasiform water and liquid water in solution. The critical relative humidity is the relative humidity of the surrounding air in equilibrium with the saturated solution of drug at a given temperature.⁶ Accordingly, there are two methods to determine the critical relative humidity. 1) The method of the balance curve of humidity adsorption⁵ and 2) method of weight change of saturated solution.⁶ The former is based on definition 1 and the latter on 2. Definition 2 is in agreement with thermodynamic principle: when the relative humidity in the air in equilibrium with the saturated solution is above the *CRH*, the solution will absorb water and gain weight; when below it, the solution will lose water and weight; and when just equal to it, the solution will neither absorb nor lose water and keep its weight constant.

The critical relative humidity of drug can be regarded as a thermodynamic property based on definition 2. When disregarding minor factors, the critical relative humidity of drug is closely related to the interaction between molecules of drug and water and the interaction between drug molecules. The stronger the attraction between drug and water molecules is; the more difficult water molecules escape from the solution; and therefore the lower the relative humidity of atmosphere in equilibrium with the saturated solution (*i.e.* the *CRH* of the drug) is. On the other hand, the stronger the attraction between drug molecules is; the relatively lower the attraction between drug and water molecules will be; and therefore the higher the *CRH* of the drug is.

The above analogy can similarly be applied to the solubility of drug in the water. The stronger the attraction between

molecules of drug and water is, the higher the solubility is; the stronger the attraction between drug molecules is, the lower the solubility is. So we believe that the higher the solubility is; the lower the *CRH* will be, and *vice versa*.

This implies that there is a certain relationship between the critical relative humidity and the solubility. The critical relative humidity could be calculated from the solubility if we can find out this relationship. This will make it possible to obtain the *CRH*, which is difficult to measure, by measuring the solubility which is relatively easy. This study is important in both application and theory about solutions and it is not found in literatures.

The relationship between the reported critical relative humidity and the solubility, expressed as the total ionic mole fraction (x_B) after ionization, of 21 electrolytes is listed in Table 1 (columns 3 and 4) and shown in Fig. 1. A negative correlation is found from the figure between the critical relative humidity and the solubility, which agrees with the above idea about the molecular interaction.

To demonstrate our hypothesis, 21 electrolytes were selected to calculate their critical relative humidity with Raoult's law, modified Debye–Hückel theory and extended NRTL (extended non-random two liquid) model from their solubility. The results indicate the critical relative humidity calculated with extended NRTL model is comparable to these in literatures.

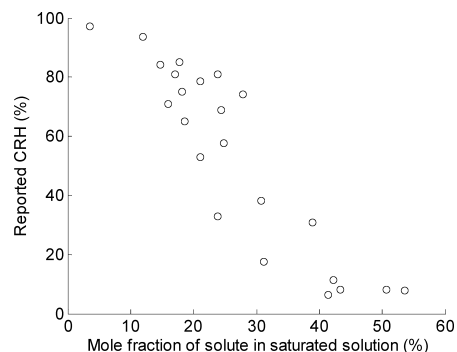


Fig. 1. The Relationship between *CRH* and Solubility of 21 Electrolytes

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Table 1. Calculated and Reported *CHR* of 21 Electrolytes

	Solubility expressed as m (mol/kg)	Solubility expressed as x_B (%)	<i>CHR</i> (reported by literature) (%)	<i>CHR</i> (calculated by Raoult's law) (%)	<i>CHR</i> (calculated by modified D-H model) (%)	<i>CHR</i> (calculated by extended NRTL model) (%)
NaCl	6.1583	18.14	75.3 ¹³⁾	81.86	71.98	75.1
KBr	5.7227	17.09	80.7 ¹³⁾	82.91	74.33	78.8
LiCl	20.1227	42.43	11.1 ¹³⁾	57.57	11.77	2.3
NH ₄ Cl	7.3742	21.07	78.6 ⁴⁾	78.93	65.01	77.1
KI	8.9398	31.14	68.9 ⁴⁾	68.86	56.60	68.9
KCl	4.7887	14.72	84.3 ¹³⁾	85.28	79.29	84.3
KNO ₃	3.7685	11.95	92.5 ¹³⁾	88.05	84.51	92.8
NaNO ₃	10.7301	27.87	73.8 ¹³⁾	72.13	47.06	74.53
LiI	12.5593	31.14	17.5 ⁴⁾	68.86	38.04	21.6
NaOH	28.525	50.67	8.24 ⁴⁾	49.33	2.12	0.1
KOH	21.2121	43.35	8.23 ⁴⁾	56.65	9.93	1.7
LiBr	19.6212	41.40	6.37 ⁴⁾	58.60	13.32	1.2
KF	17.6774	38.89	30.85 ⁴⁾	61.11	18.14	21.0
NaI	12.3020	30.7	38.4 ¹³⁾	69.30	39.26	33.7
NaBr	9.1792	24.83	57.7 ¹³⁾	75.17	55.33	56.2
MgCl ₂	5.7977	23.89	32.8 ⁴⁾	76.11	45.37	33.2
Mg(NO ₃) ₂	4.8142	21.04	52.9 ⁴⁾	78.96	56.17	60.5
SrCl ₂	3.5183	15.91	70.9 ⁴⁾	84.09	71.08	70.9
Sr(NO ₃) ₂	3.9400	17.78	85.1 ⁴⁾	82.22	66.94	87.8
K ₂ SO ₄	0.6886	3.6	97.3 ¹³⁾	96.40	96.59	97.5
(NH ₄) ₂ SO ₄	5.8044	23.89	81.1 ¹³⁾	76.11	45.37	80.2

The calculation is programmed by us with the software Matlab 7.0.

Results and Discussions

The solubility of 21 electrolytes at 25 °C can be found in the literature.⁷⁾ When the solubility at 25 °C can not be found, it can be calculated from these at temperatures 0, 10, 20, 30, 40 °C with cubic spline interpolation.⁸⁾ The molality is converted from the solubility by Eq. 1:

$$m = \frac{10S}{M_{M_v A_v}} \quad (1)$$

where m is the molality, S is the solubility (expressed as gram of solute per 100 g of water), $M_{M_v A_v}$ is the molecular weight of electrolytes.

Calculating *CHR* from Solubility According to Raoult's Law According to Raoult's law, in an aqueous solution, the vapor pressure of water in equilibrium with the solution is proportional to the mole fraction of water and can be expressed as:

$$p_A = p_A^* x_A \quad \text{or} \quad p_A/p_A^* = x_A \quad (2)$$

where p_A is the vapor pressure of water, the constant of proportionality p_A^* is the vapor pressure of pure water, x_A is the mole fraction of water and is also the relative humidity (p_A/p_A^*) of the atmosphere in equilibrium with the solution. When the solution is saturated, x_A is just the critical relative humidity of the electrolyte:

$$CHR = p_A/p_A^* = x_A \quad (3)$$

If the electrolyte with the molecular formula $M_{v_+} A_{v_-}$ is ionized completely in water, the mole fraction of water is:

$$x_A = \frac{n_A}{n_A + v n_B} \quad (4)$$

where n_A and n_B are the mole numbers of water and the electrolyte in the solution respectively, v_+ , v_- , and v are the num-

bers of positive, negative, and total ions in a molecule ($v = v_+ + v_-$).

The mole fraction of water in the saturated solution, *i.e.* the critical relative humidity of the electrolyte, was calculated according to Raoult's law, and is compared with that reported in literatures. The result is plotted in Fig. 2 and listed in Table 1 (columns 4 and 5).

The data points in the Fig. 2 are the *CHR* values calculated by Raoult's law (vertical coordinates) *vs.* the reported ones (abscissa). If the solutions followed Raoult's law (*i.e.*, they were ideal solutions), all the points would be in the straight line. Actually, it is seen from Fig. 2 most of the points are above the straight line, which indicates the calculated values are higher than the reported ones and there is a systematic error especially in low critical relative humidity range (*i.e.*, in high concentration range). It is simply because Raoult's law is a limiting law applied to ideal solution or diluted solution. The electrolyte solution is usually non-ideal solution and there are various complex interactions among the particles in the solution and therefore we can not expect Raoult's law well accords with the electrolyte solution.

Calculating *CHR* from Solubility According to Modified Debye-Hückel Theory Raoult's law can not well accord with most of the electrolyte solutions because of the neglect of the activity coefficient of water which is closely related to the interactions among the particles. In a real solution the activity of water should be used instead of the mole fraction of water, then Raoult's law can be expressed as, $p_A = p_A^* a_A$, combine it and the equation $CHR = p_A/p_A^*$, yields:

$$CHR = p_A^* a_A / p_A^* = a_A \quad (5)$$

where a_A is the activity of water. Equation 5 indicates the activity of water is just the critical relative humidity of the electrolyte.

The standard state of the solvent is pure water and the activity coefficient is 1 for pure water; the standard state of the electrolyte is infinite dilution and the activity coefficient for

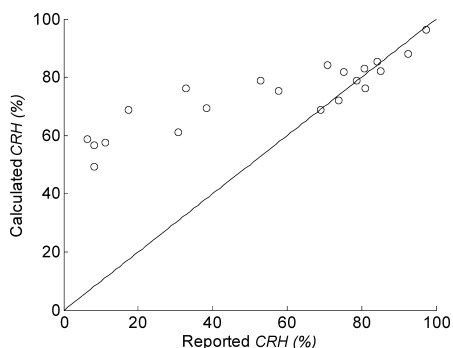


Fig. 2. The Comparison of the CRH Calculated by Raoult's Law and That Reported by Literature

the electrolyte is 1 at infinite dilution.

The aqueous solution of electrolytes is not ideal solution. Electrolyte is dissociated and yields positive and negative ions in water. The interactional electrostatic force which is inversely proportional to the square of the distance between two ions and can operate at long-range distance is called long-range electrostatic interaction. The modified Debye-Hückel theory is responsible for this interaction.

In order to reduce the deviation from real solution, Debye and Hückel⁹⁾ proposed Debye-Hückel limiting theory. It is assumed that in dilute solutions the electrical interaction is solely responsible for the deviation from real solution. In aqueous solution at 25 °C, the mean ionic activity coefficient is expressed as $\ln \gamma_{\pm} = -1.1709 |z_+ z_-| I^{0.5}$ by Debye and Hückel, where I is the ionic strength, $I = (1/2)(z_+^2 v_+ + z_-^2 v_-)m$, z_+ and z_- are the positive and negative ion charges.

Latter, based on the assumption that there is fixed distance of closest approach and real feature of the solution, Debye-Hückel equation was modified as^{7,10)}:

$$\ln \gamma_{\pm} = -\frac{1.1709 |z_+ z_-| I^{0.5}}{1 + I^{0.5}} + 0.2I \tag{6}$$

where γ_{\pm} is the mean ionic activity coefficient.

In ideal solution, the activity of the solvent is the mole fraction of the solvent. In real solutions, we define the osmotic coefficient ϕ as¹¹⁾:

$$\phi = -\frac{\ln a_A}{M_A v m} \tag{7}$$

where x_B is the mole fraction of the solute, γ_A is the activity coefficient of water in the aqueous solution.

Combining Eq. 7 and the Gibbs-Duhem equation $x_A d \ln \gamma_A + x_B d \ln \gamma_B = 0$ yields:

$$\phi = 1 + \frac{1}{m} \int_0^m m d \ln \gamma_{\pm} \tag{8}$$

Then, combining Eqs. 6 and 8 and after integrating:

$$\phi = 1 + 0.1zm + \frac{-1.1709 |z_+ z_-| \sqrt{zm}}{1 + \sqrt{zm}} - \frac{-2.3417 |z_+ z_-|}{zm} \left(\frac{zm}{2} - \sqrt{zm} + \ln(1 + \sqrt{zm}) \right) \tag{9}$$

where $z = (1/2)(z_+^2 v_+ + z_-^2 v_-)$. The osmotic coefficient can be calculated according to Eq. 9, and then the activity of water

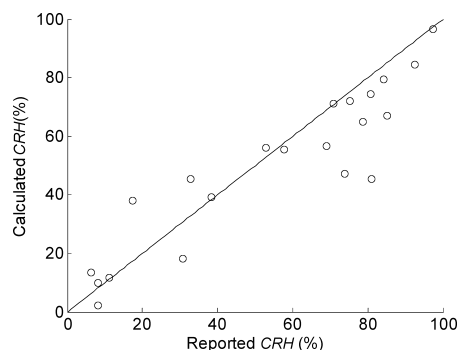


Fig. 3. The Comparison of the CRH Calculated by Modified Debye-Hückel Theory and That Reported by Literature

in the saturated solution (*i.e.*, the critical relative humidity) can be obtained by Eq. 10 which is rearranged from Eq. 7:

$$a_A = \exp(-\phi M_A v m) \tag{10}$$

The critical relative humidity of electrolyte was calculated and compared with reported one, the result is shown in Fig. 3 and listed in Table 1 (columns 4 and 6).

Although the points in Fig. 3 are in disorder, they are approximately distributed on both sides of the straight line. Compared with Raoult's law, modified Debye-Hückel theory decreases the systematic error; compared with the reported value, these calculated by the theory still have large error sometimes. Modified Debye-Hückel model is an early theory about the activity coefficient of electrolyte solution. It is simple and without characteristic parameter for each electrolyte. According to this theory, the activity of water in saturated solutions (*i.e.* the CRH of electrolytes) may be obtained by Eqs. 9 and 10 provided the solubility of electrolyte, the ion charges and the numbers of ions are known. However, this theory is only responsible for the electrostatic interaction between the ions and ignores the other interactions among the solute, solvent and so on. It is only used in dilute solution. Even so, it points out the direction for our farther research.

Calculating CRH from Solubility According to Extended NRTL Model The relationship between the critical relative humidity and the solubility is liquid-gas equilibrium and should be resolved by the principle of thermodynamics. If the gas is regarded as ideal gas, the vapor pressure of water in equilibrium with the solution can be expressed as:

$$p_A = p_A^* a_A = p_A^* \gamma_A x_A \tag{11}$$

Combining Eq. 11 and Eq. 5, yields:

$$CRH = a_A = p_A / p_A^* = \gamma_A x_A \tag{12}$$

In extended NRTL model, the excess Gibbs energy of an electrolyte solution is represented by a sum of the contributions of a long-range electrostatic interaction term represented by the Debye-Hückel model and a short-range interaction. The expression based on the local composition concept is employed to account for the short-range interactions in extended NRTL. Similarly to modified Debye-Hückel model, the standard states are considered to be pure solvent for the solvent and infinite dilution for solute. The short-range interactions, which can only operate in a short range distance, include in solvent-solvent, solvent-ion, and non-electrostatic ion-ion interactions.

The extended NRTL model used in the article was proposed by Rahmat Sadeghi in 2006¹²⁾ with a high accuracy and simple calculation. The activity coefficient of electrolytes in aqueous solution is represented by a sum of the contribution of a long-range and a short-range interaction term:

$$\ln \gamma_i = \ln \gamma_i^{\text{LR}} + \ln \gamma_i^{\text{SR}} \quad (13)$$

where the subscript i represents for the species i in the solution, $\ln \gamma_i^{\text{LR}}$ is the long-range interaction term in the activity coefficient and $\ln \gamma_i^{\text{SR}}$ is the short-range one.

In aqueous solution at temperature 298.15 K, and if the closest approach parameter of the ions is regarded as a constant value of 14.9,¹²⁾ the long-range interaction term in the activity coefficient can be expressed as:

$$\ln \gamma_A^{\text{LR}} = 5.8247 \frac{I_x^{1.5}}{1 + 14.9 I_x^{0.5}} \quad (14)$$

where $I_x = (1/2)(z_+^2 x_+ + z_-^2 x_-)$ is the ionic strength in mole fraction scale.

The short-range term of water in activity coefficient can be expressed as:

$$\begin{aligned} \ln \gamma_A^{\text{SR}} &= \frac{E_{\text{ca,m}} \ln \left[\frac{x_A + (X_+ + X_-) H_{\text{ca,m}}}{x_A + X_+ + X_-} \right]}{\ln H_{\text{ca,m}}} + \frac{x_A E_{\text{ca,m}} \left[1 - \frac{x_A + (X_+ + X_-) H_{\text{ca,m}}}{x_A + X_+ + X_-} \right]}{\ln H_{\text{ca,m}} [x_A + (X_+ + X_-) H_{\text{ca,m}}]} \\ &\times \frac{X_+ E_{\text{m,ca}} \left(H_{\text{m,ca}} - \frac{X_- + x_A H_{\text{m,ca}}}{x_A + X_-} \right)}{\ln H_{\text{m,ca}} (X_- + x_A H_{\text{m,ca}})} + \frac{X_- E_{\text{m,ca}} \left(H_{\text{m,ca}} - \frac{X_+ + x_A H_{\text{m,ca}}}{x_A + X_+} \right)}{\ln H_{\text{m,ca}} (X_+ + x_A H_{\text{m,ca}})} \\ &+ x_A E_{\text{m,ca}} \left[\frac{X_+}{(X_- + x_A)^2} + \frac{X_-}{(X_+ + x_A)^2} \right] - E_{\text{m,ca}} \left[\frac{X_+}{X_- + x_A} + \frac{X_-}{X_+ + x_A} \right] \end{aligned} \quad (15)$$

where X_+ and X_- is the effective mole fraction of positive and negative ion respectively, $X_+ = z_+ x_+$, $X_- = z_- x_-$, $x_+ = v_+ m / (55.49 + v m)$, $x_- = v_- m / (55.49 + v m)$ are the mole fractions of positive and negative ions respectively, $H_{\text{ca,m}} = \exp(-E_{\text{ca,m}}/10 + \kappa_{\text{ca,m}}/RT)$, $H_{\text{m,ca}} = \exp(-E_{\text{m,ca}}/10 + \kappa_{\text{m,ca}}/RT)$. $E_{\text{m,ca}}$, $E_{\text{ca,m}}$, $\kappa_{\text{m,ca}}/RT$ and $\kappa_{\text{ca,m}}/RT$ are four adjustable energy parameters for different electrolyte which can be found in the literature¹²⁾ and are listed in Table 2. The 21 electrolytes were selected only because their *CHR*, solubility and the energy parameters can be found in the literature.

After calculating the activity coefficient of water γ_A according to Eq. 13, the activity of water in saturated solution (*i.e.* the critical relative humidity) can be simply obtained from Eq. 12. The results are compared with those reported in literatures and are shown in Fig. 4 and listed in Table 1 (columns 4 and 7).

The data points in the Fig. 4 are approximately in the straight line, especially in high *CRH* range (>50%). This indicates that the result obtained from extended NRTL theory is much more accurate than those from modified Debye–Hückel theory because of the consideration of the short-range term in extended NRTL model. Also it is seen from Fig. 4 that the calculated *CRH* is not well comparable to the reported one in low *CRH* range (<50%, even so, it is still better than modified Debye–Hückel model).

Table 2. Energy Parameter Used in the Article¹²⁾

	$E_{\text{m,ca}}$	$\kappa_{\text{m,ca}}/RT$	$E_{\text{ca,m}}$	$\kappa_{\text{ca,m}}/RT$
NaCl	-4.856	22.968	1.084	0.055
KBr	-5.831	29.847	-0.089	2.147
LiCl	-70.752	35.451	-10.155	2.902
NH ₄ Cl	2.483	-127.048	0.785	-12.87
KI	-2.026	9.764	1.585	-1.544
KCl	-6.234	30.047	-0.089	2.147
KNO ₃	0.024	-9.541	3.356	0.102
NaNO ₃	-2.348	0.233	-5.831	-2.835
LiI	-17.127	100.078	0.201	7.394
LiBr	38.992	51.922	3.208	499.84
KF	-8.052	30.75	0.025	1.651
NaI	-9.978	48.524	0.512	2.728
NaBr	-8.868	40.414	0.403	2.183
NaOH	-11.526	52.744	-0.012	3.609
KOH	1.849	15.87	0.907	115.09
MgCl ₂	-7.347	41.391	1.233	1.417
Mg(NO ₃) ₂	-5.299	27.902	1.364	0.163
SrCl ₂	-4.621	28.602	1.691	-0.084
Sr(NO ₃) ₂	-0.523	4.35	2.593	-3.01
K ₂ SO ₄	0.331	0.039	0.486	-13.89
(NH ₄) ₂ SO ₄	-2.184	0.407	-7.011	-4.37

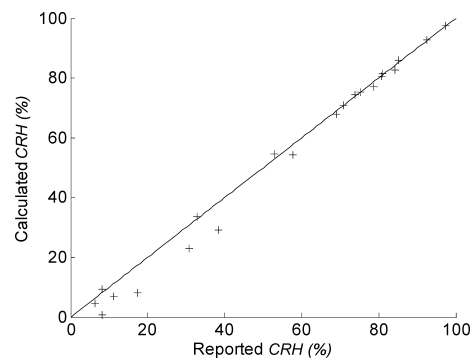


Fig. 4. The Comparison of the *CRH* Calculated by Extended NRTL Theory and That Reported by Literature

Conclusion

The authors calculate the critical relative humidity of 21 electrolytes from their solubilities in the light of Raoult's law, modified Debye–Hückel model and NRTL model. The results indicate that the critical relative humidity values calculated by Raoult's law can not accord with the reported ones and there is a systematic error in high concentration range; the values calculated by modified Debye–Hückel model still can not accord with the reported ones well although without systematic error; and the values calculated by extended NRTL are comparable to the reported ones.

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References

- 1) Young J. F., *J. Appl. Chem.*, **17**, 241–245 (1967).
- 2) Labuza T. P., Acott K., Tatini S. R., Lee R. Y., Flink J., Mccall W., *J. Food Sci.*, **41**, 910–917 (1976).
- 3) Byrn S. R., Xu W., Newman A. W., *Adv. Drug Deliv. Rev.*, **48**, 115–136 (2001).
- 4) Greenspan L., *J. Res. Nat. Bur. Stand.—A Physics and Chemistry*, **81**, 89–96 (1977).
- 5) Cui F., editor in chief, "Pharmaceutics," 5th ed., People's Health Press, Beijing, 2003, p. 301.

- 6) Wang Y., Li S., Zhang W., Wang A., *Chin. J. Pharm.*, **28**, 223—224 (1989).
- 7) “Lang’s Handbook of Chemistry,” 2nd ed., ed. by Dean J. A., translated by Wei J.-F., China Science Press, Beijing, 1988, 5.1.
- 8) Wang N., “Computational Methods—Arithmetic Design and MATLAB Implement,” 1st ed., Higher Education Press, Beijing, 2005, pp. 31—35, 195—197.
- 9) Debye P., Hückel E., *Physikalische Zeitschrift (Phys. Z)*, **24**, 185—206 (1923).
- 10) “Physical Chemistry,” 4th ed., ed. by Ying H., editor in chief, Higher Education Press, Beijing, 1999, p. 122.
- 11) Chen X., Cai Z., Hu W., “Chemical Engineering Thermodynamics,” 2nd ed., Chemical Industry Press, Beijing, 2005, p. 194.
- 12) Sadeghi R., *Fluid Phase Equilibria*, **243**, 92—100 (2006).
- 13) Opila R. L. Jr., Weschler C. J., Schubert R., *IEEE Transactions on Components Hybrids and Manufacturing Technology*, **12**, 114—120 (1989).