

# Aqueous solubility of a diatomic molecule as a function of its size & electronegativity difference

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**Abstract** The aqueous solubility of a diatomic molecule as a function of its size & electronegativity difference is investigated. The electronegativity of a diatomic molecule will be calculated using five different electronegativity scales, namely, Pauling [1], Allred-Rochow [2], Mulliken [3, 4], Parr-Yang [5], and Sanderson [6, 7]. It is hypothesized here that at a given pH, temperature, and pressure, the solubility of a diatomic molecule in water will be a function of its polar character; in particular, electronegativity difference and of its molecular size. Different forms of the solubility function were tested; it was found that the solubility model, given by Eq. 3, which is based on different electronegativity scales and the molecular volume, adequately describes the aqueous solubility of alkali halides. The aqueous solubility of alkali halides exhibits maximum at the condition of high electronegativity difference and large molecular volume. On the other hand, the minimum solubility region is observed at very low molecular volume and medium to slightly high values of electronegativity difference. The minimum solubility is also observed at low value of electronegativity difference and high molecular volume. Finally, the general trend of solubility of alkali halides, based on the proposed model (Eq. 3) could be explained in terms of the trade-off between electrostatic interactions (solid lattice side) and the entropic effects (water side).

**Keywords** Inter-ionic volume · Polarity · Aqueous solubility · Electronegativity · Mono-valent · Alkali halides · Electrostatic interactions · Entropic effects

## Introduction

Noorizadeh and Shakerzadeh [8] proposed an estimation for the bond dissociation energies of some diatomic molecules (in both covalent and ionic forms) using different formulas and a new scale of electronegativity. The calculated bond dissociation energies were compared with those which were obtained from the other commonly used electronegativity scales such as Pauling [1] and Allred-Rochow [2]. The best linear correlation was observed between the obtained bond dissociation energies from new electronegativity scale and experimental data. Comparison between the corrected results, which were calculated from the linear relationship equations for different scales, showed that in both covalent and ionic bonds the new scale of electronegativity represented a better correlation with the experimental data than the others.

Smith [9] discussed the limitation of Pauling's equation regarding the calculation of electronegativity of either homo- or hetero-polar bonds. The fact that Pauling [1]'s equation underestimates the electronegativity for molecules formed by the least electronegative elements, and overestimates that for fluorides of most metallic elements, led Smith to introduce a two-parameter model that will better estimate the electronegativity for such anomalies. The first parameter is a quantity linearly related to electronegativity in the Mulliken [3, 4] and Pauling [1] sense and the second term is related to the intrinsic bonding potential of an atom, which is primarily related to atomic size, and to the suitability in energy and radial extension of its valence orbitals.

Politzer and Murray [10] confirmed the link between the first ionization energy ( $I_1$ ) and electron affinity ( $A$ ) of an atom on one side and its electronegativity ( $\chi$ ) and hardness ( $\eta$ ) on another side. Their analysis provided some support for the validity of the widely-used electronegativity and

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hardness formulas  $\chi = 0.5(I_1 + A)$  and  $\eta = 0.5(I_1 - A)$ , for the atoms in Groups IIIA and IVA – VIIIA; oxygen being an exception.

In the present article, the aqueous solubility of a diatomic molecule as a function of its size & electronegativity difference is investigated. The electronegativity difference of a diatomic molecule will be calculated using five different electronegativity scales, namely, Pauling [1], Allred-Rochow [2], Mulliken [3, 4], Parr-Yang [5], and Sanderson [6, 7].

## Theory

It is hypothesized here that at a given pH, temperature, and pressure, the solubility of a diatomic molecule in water will be a function of its polar character; in particular, electronegativity and of its molecular size. Different models were proposed to calculate the electronegativity of elements (See the above cited literature). Table 1 shows five different scales of electronegativity as proposed by different investigators.

The molecular size was calculated using the following equations:

$$r = \frac{r^+ + r^-}{2} \quad (1)$$

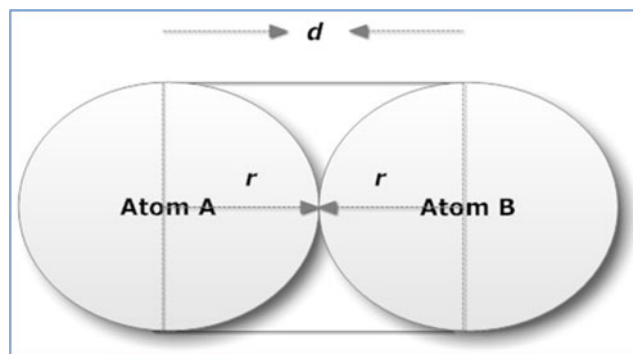
$$V_{molecule} = \frac{4}{3}\pi r^3 + \pi r^2 d \quad (2)$$

where  $V_{molecule}$  is the molecular volume of a diatomic molecule based on inter-ionic radii of the composing ions.

**Table 1** Electronegativity\* of elementary atoms using five different models

Atom	Atomic Number	X <sub>Paul</sub>	X <sub>P-Y</sub>	X <sub>A-R</sub>	X <sub>Mull</sub>	X <sub>Sndr</sub>
Li	3	0.98	3.00	0.97	0.97	0.89
O	8	3.44	7.54	3.5	3.41	3.65
F	9	3.98	10.41	4.1	3.91	4
Na	11	0.93	2.84	1.01	0.91	0.56
S	16	2.58	6.22	2.44	2.69	2.96
Cl	17	3.16	8.29	2.83	3.1	3.48
K	19	0.82	2.42	0.91	0.73	0.45
Cu	29	1.9		1.75	1.49	1.98
Br	35	2.96	7.58	2.74	2.95	3.22
Rb	37	0.82	2.33	0.89	0.69	0.31
Ag	47	1.93		1.42	1.47	1.83
I	53	2.66	6.75	2.21	2.74	2.78
Cs	55	0.79	2.18	0.86	0.62	0.22
Ba	56	0.89	2.68	0.97	0.88	0.68
Au	79	2.54		1.42	1.87	

\* Ref: [1, 2, 3, 4, 5], and [6, 7]



**Fig. 1** A schematic showing how the molecular volume of a diatomic molecule is calculated in terms inter-ionic radii

Since, in general, the ionic radius of both ions will be different, the arithmetic average of the two ionic radii,  $r$ , is considered in Eq. 1 and  $d$  is equal to  $2r$ . Equation 2 approximates the molecule as a rod with two rounded ends each has a diameter equal to  $2r$  and the length of the rod is equal to the inter-nuclear distance,  $d$ . See Fig. 1. In words, Eq. 2 says that the volume of a diatomic molecule is equal to two hemispheres (*i.e.*, one sphere) plus a cylinder with radius  $r$  and length  $d$ .

The ionic radii of species used in our study are shown in Table 2. The solubility data for some diatomic compounds are shown in Table 3.

## Results and discussion

The electronegativity difference of a diatomic molecule was calculated based on the electronegativity difference between atoms making up the molecule. Table 3 shows the results for electronegativity difference using five different electronegativity scales. Null values present in Table 3

**Table 2** Ionic radii\* of species used in this study

Species	r(A°)	Species	r(A°)
Br <sup>-</sup>	1.96	Ba <sup>++</sup>	1.3
Cl <sup>-</sup>	1.81	Cs <sup>+</sup>	1.65
F <sup>-</sup>	1.33	Cu <sup>+</sup>	0.96
I <sup>-</sup>	2.2	K <sup>+</sup>	1.33
O <sup>-2</sup>	1.32	Li <sup>+</sup>	0.78
S <sup>-2</sup>	1.74	Na <sup>+</sup>	0.98
Ag <sup>+1</sup>	1.13	Rb <sup>+</sup>	1.49
Au <sup>+</sup>	1.37		

\*Ref: J.F. Shackelford and W. Alexander [11]

**Table 3** Electronegativity difference for atoms making up the diatomic molecule, based on five different electronegativity scales, the solubility data\*, and the molecular volume, expressed in cubic Angstrom, ( $\text{\AA}^3$ )

Species	$\Delta X_{\text{Paul}}$	$\Delta X_{\text{P-Y}}$	$\Delta X_{\text{A-R}}$	$\Delta X_{\text{Mull}}$	$\Delta X_{\text{Sndr}}$	Solubility g/100g water @20°C	Solubility g/100g water @25°C	$d(\text{\AA})$	$V_{\text{molecule}} (\text{\AA}^3)$
AgBr	1.03		1.32	1.48	1.39		0.000014	3.09	38.62
AgCl	1.23		1.41	1.63	1.65		0.00019	2.94	33.26
AgF	2.05		2.68	2.44	2.17		63.23	2.46	19.49
AgI	0.73		0.79	1.27	0.95		0.000003	3.33	48.34
AgO	1.51		2.08	1.94	1.82		0.0027	2.45	19.25
AuCl	0.76		1.41	1.23		0.000031		3.18	42.09
BaO	2.55	4.86	2.53	2.53	2.97	1.48		2.62	23.54
BaS	1.69	3.54	1.47	1.81	2.28	6.97	8.21	3.04	36.77
CsBr	2.17	5.40	1.88	2.33	3		55.2	3.61	61.58
CsCl	2.37	6.11	1.97	2.48	3.26	64.96	65.64	3.46	54.22
CsF	3.19	8.23	3.24	3.29	3.78		85.1	2.98	34.64
CsI	1.87	4.57	1.35	2.12	2.56	43.2	45.9	3.85	74.70
CuBr	1.06		0.99	1.46	1.24	0.0012		2.92	32.59
CuCl	1.26		1.08	1.61	1.5	0.0047		2.77	27.82
CuI	0.76		0.46	1.25	0.8	0.00002		3.16	41.30
KBr	2.14	5.16	1.83	2.22	2.77	39.4	40.4	3.29	46.61
KCl	2.34	5.87	1.92	2.37	3.03	25.39	26.22	3.14	40.52
KF	3.16	7.99	3.19	3.18	3.55	47.3	50.41	2.66	24.64
KI	1.84	4.33	1.3	2.01	2.33	59	59.7	3.53	57.58
LiBr	1.98	4.58	1.77	1.98	2.33	62.7	64.4	2.74	26.93
LiCl	2.18	5.28	1.86	2.13	2.59	45.29	45.81	2.59	22.74
LiF	3	7.40	3.13	2.94	3.11	0.131	0.134	2.11	12.30
LiI	1.68	3.75	1.24	1.77	1.89	61.7	62.3	2.98	34.64
NaBr	2.03	4.74	1.73	2.04	2.66	47.7	48.6	2.94	33.26
NaCl	2.23	5.44	1.82	2.19	2.92	26.41	26.45	2.79	28.43
NaF	3.05	7.56	3.09	3	3.44	3.89	3.97	2.31	16.13
NaI	1.73	3.91	1.2	1.83	2.22	63.9	64.8	3.18	42.09
RbBr	2.14	5.25	1.85	2.26	2.91	52.6	53.8	3.45	53.75
RbCl	2.34	5.95	1.94	2.41	3.17	47.53	48.42	3.3	47.04
RbF	3.16	8.07	3.21	3.22	3.69	75		2.82	29.35
RbI	1.84	4.42	1.32	2.05	2.47	61.1	62.3	3.69	65.77

\*Quoted from D.R. Lide [12], p.4-37–p.4-111

**Table 4** Statistical parameters associated with the solubility model (Eq. 3) for all diatomic molecules shown in Table 3. Solubility data are @ 20 °C

Electro-negativity Scale	SSE♦	$R^2$	# of Observations	D.o.F*	RMSE <sup>+</sup>
Pauling	8741	0.4605	24	19	21.45
Parr-Yang	5555	0.4649	20	15	19.24
Allred-Rochow	10896	0.3274	24	19	23.95
Mulliken	8496	0.4756	24	19	21.15
Sanderson	9191	0.3846	23	18	22.60

♦ SSE: Sum of Square Errors =  $\sum_{i=1}^N (Z_{\text{exp}} - Z_{\text{fit}})^2$ 

\*D.o.F.: Degree of Freedom = # of data points–# of model parameters

<sup>+</sup> RMSE: Root Mean Square Error =  $\sqrt{\frac{\text{SSE}}{\text{D.o.F}}}$ **Table 5** Statistical parameters associated with the solubility model (Eq. 3) for all diatomic molecules shown in Table 3. Solubility data are @ 25 °C

Electro-negativity Scale	SSE	$R^2$	# of Observations	D.o.F	RMSE
Pauling	9881	0.4263	25	20	22.23
Parr-Yang	4393	0.5427	20	15	17.11
Allred-Rochow	11513	0.3316	25	20	23.99
Mulliken	10029	0.4177	25	20	22.39
Sanderson	10965	0.3634	25	20	23.41

means that the electronegativity scale under question does not report a value for either atom or both atoms making up the diatomic molecule. Notice that Pauling's, Allred-Rochow's, and Mulliken's electronegativity scale report values for most common elements; hence the corresponding column in Table 3 has no null values. In addition, Table 3 shows the solubility data both at 20 and 25 °C, the length,  $d=2r$ , and the molecular volume, expressed in cubic Angstrom, ( $\text{\AA}^3$ ).

The MATLAB® surface fitting tool allows the fitting of non-symmetric experimental data which may contain NAN (not a number) values as is the case in Table 3. The general formula for curve-fitting is:

$$Z = (X, Y)$$

where  $Z$  is the dependent variable and  $X$  &  $Y$  are the independent variables.

The solubility ( $Z$ ) was fitted as a function of both the molecular volume ( $X$ ) and the electronegativity difference ( $Y$ ) as given in Table 3. Different models were attempted and the best results are shown in the consecutive tables. In general, the following model was found to be the most adequate in terms of model goodness:

$$Z = a + b*X + c*Y + d*Y^2 + e*(X/Y) \quad (3)$$

Tables 4 and 5 show that, in general, the correlation coefficient,  $R^2$ , is low.

If only a monovalent diatomic molecule (*i.e.*, has a single bond or one pair of shared electrons) is considered in the analysis, the following results are obtained as shown in Table 6 and 7.

Notice the difference from the previous case (both monovalent & divalent diatomic molecules) is that there is an improvement in the model predictability using the electronegativity scale as given by Parr and Yang [5]. For other electronegativity scales, there is practically no significant improvement in the model goodness, given that the correlation coefficient,  $R^2$ , did not significantly change from the previous case.

If further refinement is done by considering only alkali-halides, the following results are obtained as shown in Tables 8 and 9. One can notice that there is now a pronounced improvement in the model goodness (or, predictability) from the previous case (monovalent diatomic molecules only) for all electronegativity models, except for Parr-Yang's which remained essentially the same as that of the monovalent case.

The curve-fitted parameters of the solubility model (Eq. 3) being applied to alkali-halides while accompanied by the 95% confidence interval are shown in Tables 10 and 11, respectively, for both 20 °C and 25 °C solubility data.

**Table 6** Statistical parameters associated with the solubility model (Eq. 3) for only a monovalent diatomic molecule. Solubility data are @ 20 °C

Electro-negativity Scale	SSE	$R^2$	# of Observations	D.o.F	RMSE
Pauling	6956	0.5082	22	17	20.23
Parr-Yang	1348	0.8136	18	13	10.18
Allred-Rochow	9312	0.3416	22	17	23.40
Mulliken	7162	0.4936	22	17	20.53
Sanderson	7398	0.4157	21	16	21.50

**Table 7** Statistical parameters associated with the solubility model (Eq. 3) for only a monovalent diatomic molecule. Solubility data are @ 25 °C

Electro-negativity Scale	SSE	$R^2$	# of Observations	D.o.F	RMSE
Pauling	9121	0.4377	24	19	21.91
Parr-Yang	1243	0.8467	19	14	9.42
Allred-Rochow	10556	0.3493	24	19	23.57
Mulliken	9373	0.4222	24	19	22.21
Sanderson	10113	0.3765	24	19	23.07

**Table 8** Statistical parameters associated with the solubility model (Eq. 3) for alkali-halides. Solubility data are @ 20 °C

Electro-negativity Scale	SSE	$R^2$	# of Observations	D.o.F	RMSE
Pauling	1506	0.7917	18	13	10.76
Parr-Yang	1348	0.8136	18	13	10.18
Allred-Rochow	2298	0.6822	18	13	13.29
Mulliken	1060	0.8535	18	13	9.03
Sanderson	2155	0.7020	18	13	12.87

**Table 9** Statistical parameters associated with the solubility model (Eq. 3) for alkali-halides. Solubility data are @ 25 °C

Electro-negativity Scale	SSE	$R^2$	# of Observations	D.o.F	RMSE
Pauling	1400	0.8274	19	14	10.00
Parr-Yang	1243	0.8467	19	14	9.42
Allred-Rochow	2299	0.7166	19	14	12.81
Mulliken	1034	0.8726	19	14	8.59
Sanderson	2054	0.7468	19	14	12.11

**Table 10** Curve-fitted parameters of the solubility model (Eq. 3), accompanied by the 95% confidence interval for monovalent alkali-halides. Data points are @ 20 °C

Electro-negativity Scale	a±95% C.I.	b±95% C.I.	c±95% C.I.	d±95% C.I.	e±95% C.I.
Pauling	927±328	7.6±2.9	-688±254	122.7±46.7	-14.7±5.9
Parr-Yang	713±230	6.2±2.3	-214±72	15.4±5.3	-28.6±11.4
Allred-Rochow	504±238	5.1±2.5	-413±208	77.9±40.3	-7.6±4.0
Mulliken	1033±291	7.9±2.8	-758±219	134.1±39.3	-15.9±6.2
Sanderson	779±366	5.4±3.5	-480±229	73.1±35.2	-13.0±9.5

Notice that all models of electronegativity scale work fine when only considering the alkali halides. This might be attributed to the fact that Pauling's equation [1] underestimates the electronegativity for molecules formed by the least electronegative elements, and overestimates that for fluorides of most metallic elements [9], then the electronegativity difference will be magnified giving rise to a more significance or weight for such a parameter in predicting the aqueous solubility of alkali halides. Other models are thought, more or less, to give the maximum electronegativity difference between an alkali and halogen element.

As shown in Figs. 2 and 3, the aqueous solubility of alkali halides, in general, exhibits maximum at the condition of high electronegativity difference and large molecular volume (right top corner of Fig. 3). The minimum solubility region is observed at very low molecular volume and medium to slightly high values of electronegativity difference. The minimum solubility is also observed at low value of electronegativity difference and high molecular volume (right bottom corner of Fig. 3).

It is thought here that the upper half of Fig. 3 represents the region where the electrostatic interactions are operative or influential (solid lattice side); on the other hand, the lower half of the figure represents the region where the entropic effects (restructure or re-order of water molecules around solute molecules) are important. The trade-off between these two factors will govern the extent of solubility of the alkali halide material in water.

*Let's start from left top and proceed clockwise.*

At left top region, as the molecular volume is low and electrostatic interactions are relatively high, then there

seems to be a sort of self-association among molecules in the crystal phase, which renders them less soluble in water phase.

At right top, as the molecular volume is large and given that the electrostatic interactions will become weak at long-range distances, the self-association among molecules in the crystal phase will be weakened which will leave the door open for molecules to be hydrated or dissolved in water.

At right bottom, although the electrostatic interactions are weak, at long-range distances, to keep solid crystal molecules tied together; however, the entropic effects are in disfavor of dissolution of large-size solute molecules. This is analogous to the case of the non-polar large-size hydrocarbon molecules being the least soluble moieties in water.

At left bottom, the electrostatic interactions are weak because the electronegativity difference is low, yet in this region, the entropic effects are not in disfavor of solubilizing small-size solute molecules. Hence, the solubility value is moderate; neither high nor low. This might explain why the solvation (or hydration) of a small-size molecule in water is larger than that of a large-size molecule both having the same polar characteristics.

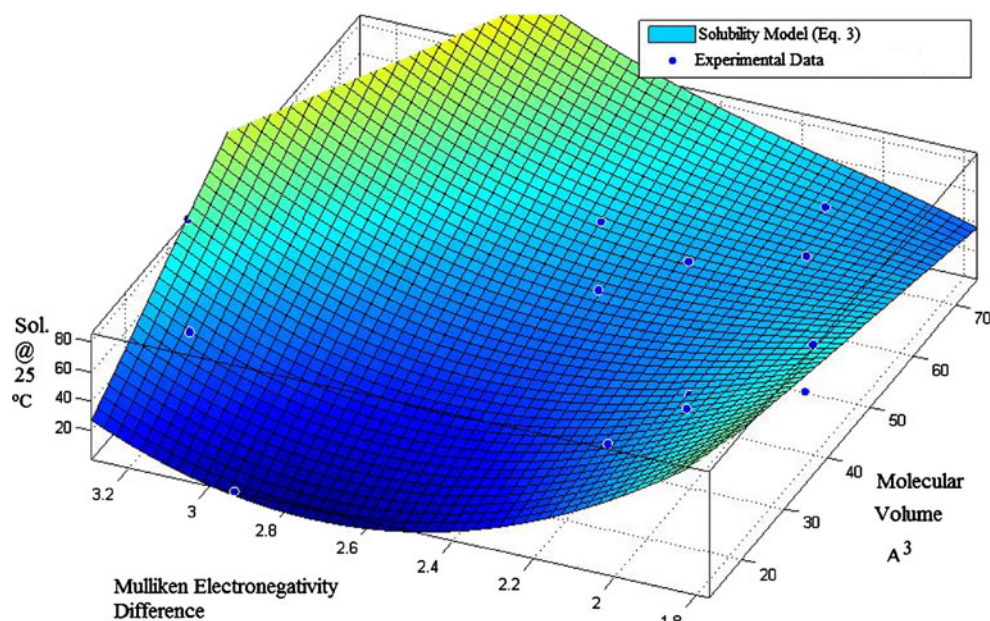
## Conclusions

1. In general, the solubility model, given by Eq. 3, which is based on different electronegativity scales and the

**Table 11** Curve-fitted parameters of the solubility model (Eq. 3), accompanied by the 95% confidence interval for monovalent alkali-halides. Data points are @ 25 °C

Electro-negativity Scale	a±95% C.I.	b±95% C.I.	c±95% C.I.	d±95% C.I.	e±95% C.I.
Pauling	900±270	7.2±2.3	-665±208	118.2±37.9	-14.1±4.8
Parr-Yang	678±186	5.8±1.8	-202±58	14.5±4.2	-26.8±9.3
Allred-Rochow	495±206	4.8±2.0	-403±177	75.8±34.0	-7.2±3.3
Mulliken	931±231	6.9±2.3	-677±171	119.0±30.7	-14.0±5.1
Sanderson	768±309	5.3±3.0	-471±190	71.4±28.7	-12.7±8.3

**Fig. 2** A typical plot for solubility at 25 °C as a function of molecular volume and the electronegativity difference as predicted by Mulliken [5, 6] for alkali halide molecules



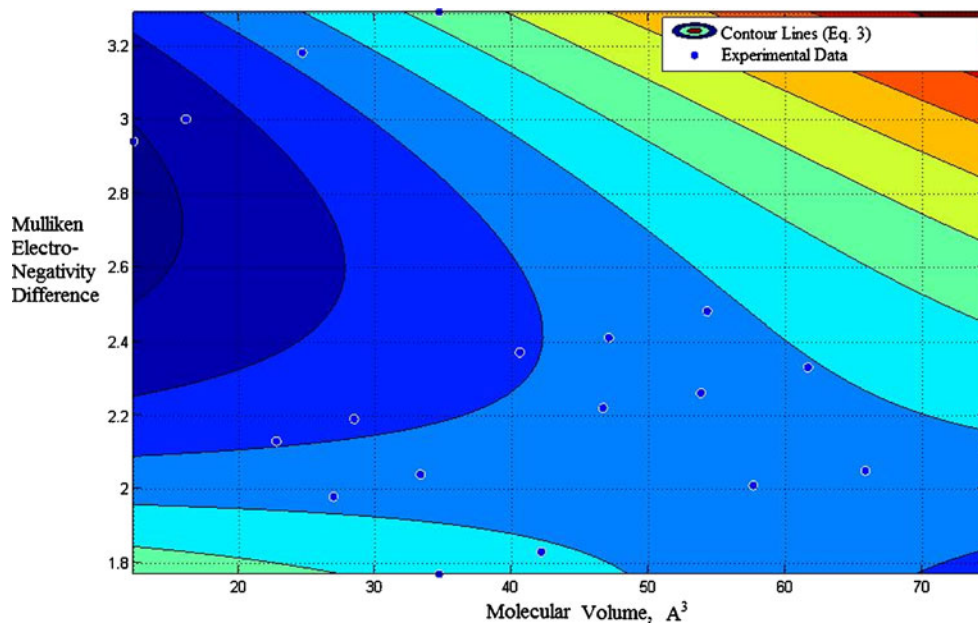
molecular volume, adequately describes the aqueous solubility of alkali halides.

2. The aqueous solubility of alkali halides exhibits maximum at the condition of high electronegativity difference and large molecular volume.
3. The minimum solubility region is observed at very low molecular volume and medium to slightly high values

of electronegativity difference. The minimum solubility is also observed at low value of electronegativity difference and high molecular volume.

4. The general trend of solubility of alkali halides, based on the proposed model (Eq. 3) could be explained in terms of the trade-off between electrostatic interactions (solid lattice side) and the entropic effects (water side).

**Fig. 3** A contour plot for the aqueous solubility at 25 °C as a function of molecular volume and the electronegativity difference as predicted by Mulliken [5, 6] for alkali halide molecules. The red zone means maximum solubility and the dark blue means minimum



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