

Thermodynamic Studies of Binary Aqueous Phosphonium Based Ionic Liquids

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Abstract

Osmotic properties of aqueous solutions play an important role in understanding intermolecular interaction between molecules and their variation with concentration. In this work, the osmotic coefficient values of aqueous solutions of phosphonium based fatty acid ILs (tetrabutylphosphonium propionate, tetrabutylphosphonium butanonate, tetrabutylphosphonium hexanoate tetrabutylphosphonium octanonate, and tetrabutylphosphonium decanonate) and amino acid based ILs (tetrabutylphosphonium glycinate, tetrabutylphosphonium valinate, tetrabutylphosphonium proliniate, and tetrabutylphosphonium threoninate) as well as tetrabutylphosphonium methanesulphonic acid obtained by vapor pressure osmometry (VPO) at 298.15 K and at atmospheric pressure are reported. From this data water activity (a_w), vapor pressure (p), mean molal activity coefficients (γ_{\pm}), Gibbs free energy of mixing (ΔG_{mix}) and excess Gibbs free energy change (ΔG^E) were calculated. The calculated activity coefficients are correlated with the McMillan-Mayer theory and the Pitzer model. The results are explained in terms of the association of ions with ILs and the structure of ILs.

Materials and methods

All the solutions were prepared on a molality basis at 298.15 K. The density measurements were made by using Rudolph Research Analytical Density meter (DDM 2911). The instruments was calibrated every time by using Millipore water and the temperature was controlled to about ± 0.01 K. All data were collected at least in triplicate and the average values are reported. The osmotic coefficients (ϕ) of aqueous ILs solutions were determined using a Knauer K-7000 vapor pressure osmometer at 298.15 K.

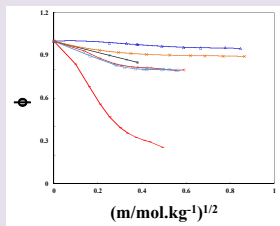
Osmotic properties of $[P_{4444}][FA]$ ILs

>The experimental osmotic coefficient (ϕ) can be expressed as

$$\ln a_w = -\phi \left(\frac{x_2}{x_1} \right)$$

>Further, a_w data was used to calculate the solvent activity coefficient (γ_1) by using the equation

$$\gamma_1 = \frac{a_w}{x_1}$$



$\Delta[P_{4444}][Pro]$,
 $\times[P_{4444}][But]$,
 $\diamond[P_{4444}][Hex]$,
 $\square[P_{4444}][Oct]$,
 $-[P_{4444}][Dec]$

>The ϕ values can be expressed as

$$\phi = 1 - \frac{2.303}{3} A_v \sqrt{m} + \sum_{i=2}^n A_i m^{i/2}$$

>The mean molal activity coefficients of ILs (γ_{\pm}) were obtained using the equation

$$\ln \gamma_{\pm} = -2.303 A_v \sqrt{m} + \sum_{i=2}^n \left[\frac{i+2}{i} \right] A_i m^{i/2}$$

>Free energy change of mixing, excess Gibbs energy and the vapour pressures (p) of solution were calculated using the equations

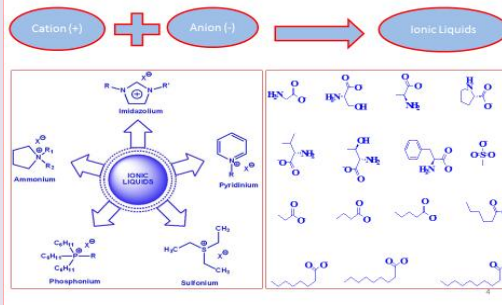
$$\Delta G_{mix} = RT[x_1 \ln a_1 + v x_2 \ln a_2] \quad \Delta G^E = RT[x_1 \ln \gamma_1 + v x_2 \ln \gamma_2]$$

$$\ln a_w = \ln \left(\frac{P}{P^*} \right) + \frac{(B - V^1)(P - P^*)}{RT}$$

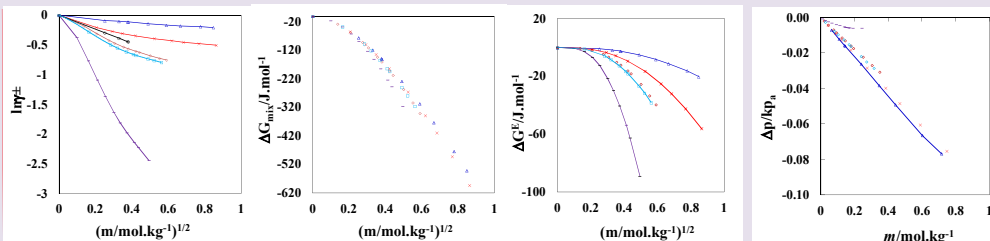
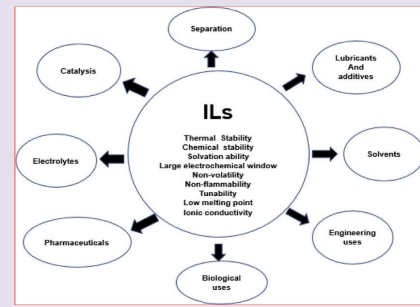
ω /kg.mol ⁻¹	A_{22}	$10^{-3} \cdot NB_{22}^0$ /mm ³ mol ⁻¹	$10^{-3} \cdot NB_{11}^0$ /mm ³ mol ⁻¹	$\beta^{(0)}$ /kg.mol ⁻¹	$\beta^{(1)}$ /kg.mol ⁻¹	C^{\dagger}	$\sigma(\phi)$
0.61	67.76	610	334	-0.69	2.52	0.55	0.0072
0.04	4.96	44	345	0.20	-0.20	-0.12	0.0010
-1.19	-132.08	-1189	376	1.99	-4.85	-2.01	0.0052
-1.53	-170.03	-1531	405	2.51	-5.94	-2.55	0.0009
-10.57	-1173.57	-10568	335	13.62	-32.57	-16.54	0.0023
-0.35	-39.74	-358	335	1.13	-2.40	-1.04	0.0043
-1.67	-186.1	-1676	377	4.85	-9.36	-6.36	0.0082
-1.35	-150.2	-1353	375	2.75	-5.85	-3.24	0.0018
-8.46	-939.5	-8461	379	28.45	-50.31	-46.95	0.0286
-2.25	-249.84	-2249	397	3.60	-8.31	-4.07	0.0035

Ionic liquids

Introduction

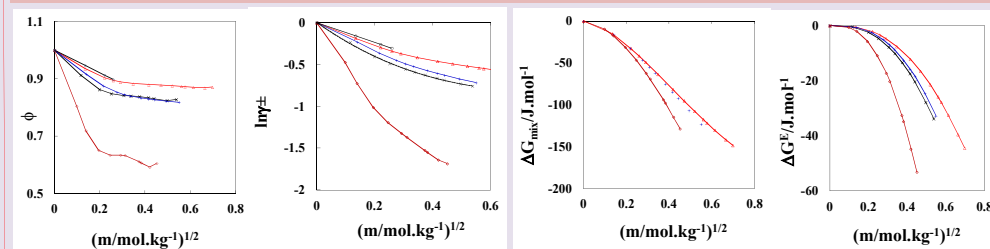


Applications of ILs



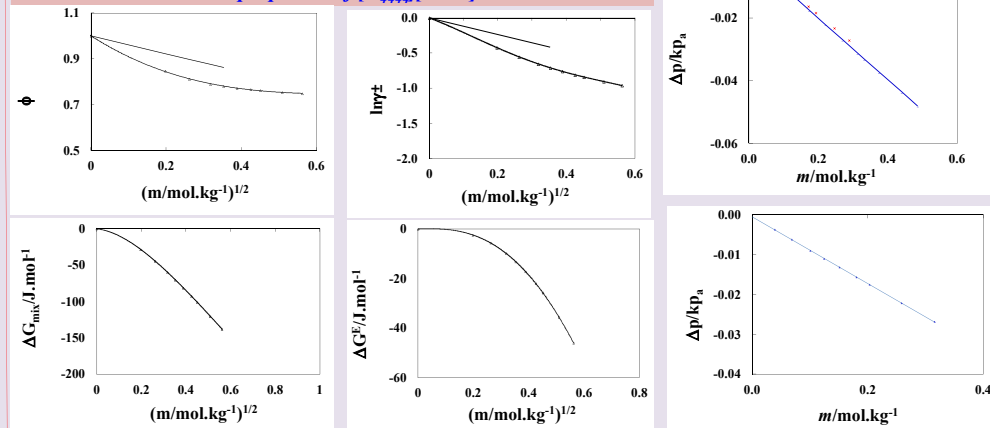
$\Delta[P_{4444}][Pro]$, $\times[P_{4444}][But]$, $\diamond[P_{4444}][Hex]$, $\square[P_{4444}][Oct]$, $-[P_{4444}][Dec]$

Osmotic properties of $[P_{4444}][AA]$ ILs



$\Delta[P_{4444}][Gly]$, $+ [P_{4444}][Val]$, $\times [P_{4444}][Pro]$, $\square [P_{4444}][Thr]$

Osmotic properties of $[P_{4444}][MSA]$ IL



Conclusions

- > Osmotic coefficients (ϕ), water activity (a_w), Gibbs free energy change of mixing (ΔG_{mix}) and the excess Gibbs free energy change (ΔG^E) decreases with increasing concentration of ILs at 298.15 K.
- > ϕ data show a negative deviations for all the amino acid ILs ($[P_{4444}][Gly]$, $[P_{4444}][Pro]$, $[P_{4444}][Val]$, $[P_{4444}][Thr]$) as well as for $[P_{4444}][Hex]$, $[P_{4444}][Oct]$, $[P_{4444}][Dec]$, and $[P_{4444}][MSA]$.
- > $[P_{4444}][Pro]$ and $[P_{4444}][But]$ show +ve deviations from DHLL where as $[P_{4444}][Pent]$, $[P_{4444}][Hex]$, $[P_{4444}][Oct]$ and $[P_{4444}][Dec]$ show -ve deviations from DHLL.
- > ΔG_{mix} and ΔG^E are both negative for all the systems studied and show deviation from Raoult's law where as ΔG_{mix} indicates spontaneous nature of mixing for all the studied ILs.
- > Vapour pressure depression study shows that as the size of anion increases the ion-solvent interaction decreases i.e. hydrophobic nature or water structure making effect increases.
- > As concentration increases IL-IL interaction increases i.e. water structure making effect increases.

References

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- Dilip H. Dagade, Poonam K. Shetake and Kesharsingh J. Patil. Thermodynamic Studies of Aqueous and CCl_4 Solutions of 15-Crown-5 at 298.15 K: An Application of McMillan-Mayer and Kirkwood-Buff Theories of Solutions. J. Phys. Chem. B 111, 26, (2007), 7610–7619