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Standard Gibbs energy of adsorption and surface properties for ionic liquids binary mixtures

Ensieh Ghasemian Lemraski *, Elham Kargar

Faculty of Science, Ilam University, PO Box 69315516, Ilam, Iran

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ABSTRACT

A classical thermodynamic model for the first time is used to derive an equation for the standard Gibbs energy of adsorption and surface properties for ionic liquids binary mixtures. Where experimental surface tension of the mixtures is available, the agreement between the calculated and the experimental data is found to be very good. Bulk mole fraction and surface tension of one of the pure component are necessary inputs for this equation. In addition, to find more information about surface structure of binary mixtures, the surface tension of binary mixtures has been studied using extended Langmuir model (EL).

1. Introduction

Ionic liquids (ILs) are salts composed of an organic cation and an inorganic anion, which are liquid at ambient conditions [1,2]. Because of their interesting physical and chemical properties such as negligible vapour pressure, unique permittivity, high thermal stability, good solubility for both organic and inorganic substances and high electrical conductivity [3–5], they offer new applications in preparative chemistry and chemical engineering as new reaction media for chemical synthesis [6], biocatalysts [7], nanomaterial technologies [8], electrochemical applications [9] and separation processes [10]. Reactions have been proposed for ILs, taking advantage of phase transitions due to changes of temperature or composition, that enable elegant separation of products, educts and catalyst. So far, most effort in ILs has been focused on the experimental and theoretical investigation of their physical and chemical properties, such as melting point, viscosity, density, thermal and electrochemical stability, solvent properties and surface tension [11–18].

The surface tension is an important property in the study of physics and chemistry at free surfaces. It affects the transfer rates of vapor absorption where a vapor–liquid interface exists. Such data are of importance to scientists, engineers and practitioners in many fields such as chemical process and reactor engineering, flow and transport in porous media, materials selection and engineering, etc. [19,20].

Recently, different models have been used to predict surface tensions of some pure ionic liquids [21–25], but a few of them studied surface tension and surface properties of ionic liquid solutions.

In this work, we propose a simple equation for predicting the surface tension of pure component, the excess surface layer and the standard Gibbs energy of adsorption of ILs binary mixtures, based on the Shereshefsky method [26].

The average relative error obtained from the comparison of experimental and calculated surface tension values for studied system show that the model has good accuracy in comparison with other predictive equations.

Finally, a new semiempirical model extended Langmuir model (i.e., EL model) was applied to analysis of surface tension for organic and aqueous solution [27–29]. In this model, the interaction of solute and solvent was evaluated by two adjustable parameters. One of them represents the lyophobicity of the components, and the other represents the effect of interaction between components.

2. Theoretical section

An alternative model that gives knowledge about the surface structure of binary solutions and is able to compute the excess number of molecular layers and free energy change in the surface region was developed by Shereshefsky[26]. Shereshefsky presented his model by assuming that the surface is homogeneous and uniform in composition and the energy of interaction between the molecules in the surface region is less than that of the bulk liquid phase due to its lower density and greater average distance between molecules. Based on these

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* Corresponding author. Fax: +98 841 2227022.
E-mail addresses: e.ghasemian@ilam.ac.ir, eghasemian@ymail.com (E.G. Lemraski).

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assumptions, Shereshefsky derived an equation for the surface tension, σ, of a binary solution as represented by the following equation:

$$\sigma = \sigma_1 - \frac{\Delta\sigma_\circ x_{2B}\, e^{\Delta G_s/RT}}{1 + x_{2B}\left(e^{\Delta G_s/RT} - 1\right)} \tag{1}$$

where $\Delta\sigma_\circ = \sigma_1 - \sigma_2$ is the difference between the surface tensions of pure solvent σ_1 and pure solute σ_2, x_{2b} is the mole fraction of solute in the bulk liquid, T is the absolute temperature and R is the gas constant. In Eq. (1), ΔG_S is the free energy change of replacing 1 mol of solvent with 1 mol of solute in the surface region.

Also, the excess number of molecular layers of solute in the surface region in respect to the bulk region δ_2^E, which has been named as number of molecular layers by Shereshefsky, is redefined here in consistency with the Gibbs equation for adsorption in the following form:

$$\delta_2^E = \frac{\Delta\sigma_\circ A_2}{\Delta G_S} \tag{2}$$

where A_2 is the molar area of solute (2). The molar area of solute (2) is given by

$$\overline{A_2} = \left({}^{M_2}\!/_{\rho_2}\right)^{2/3} N_A^{1/3} \tag{3}$$

where M_2 and ρ_2 are the molecular weight and the density of solute and N_A is Avogadro's number. A positive and high value of δ_2^E means that solute (2) is adsorbed in the surface, and therefore, solute molecules are in excess in the surface with respect to the bulk. Such a case is observed for binary solutions where an addition of the solute to the solvent the surface tension of binary solution shows a decreasing trend, whereas a negative value of δ_2^E means that solute (2) is not adsorbed in the surface and it is in excess in the bulk with respect to the surface.

Also, the standard Gibbs energy of adsorption, which reflects the energy required to move one molecule of solute from the bulk to the surface, can be expressed as [27]:

$$\Delta G^\circ = -\lim_{x_{2b}\to 0}\{RT\ln(\Delta\sigma/x_{2b})\} \tag{4}$$

Tahery et al. [30] combined Eqs. (1) and (4) to calculate standard Gibbs energy of adsorption with the following equation.

$$\frac{\Delta G^\circ}{RT} = -\left(\frac{\Delta G_s}{RT} + \ln\Delta\sigma_\circ\right) \tag{5}$$

3. Results and discussion

The surface tensions of ionic liquid binary solutions were fitted in Eq. (1) for 19 binary organic–ionic liquid solutions and 11 binary ionic liquid solutions, and results are given in Tables 1 and 2. Unfortunately, only data for some of ionic liquids binary mixtures were available, and thus, only the applicability of this prediction to the few number of ionic liquids binary mixtures could be tested. The absolute average deviation percent (RAD%) in the surface tension of solute is calculated by the following equation and are given in Tables 1 and 2:

$$\mathrm{RAD\%} = 100 \times \left|\left(\frac{\sigma_{i,\exp} - \sigma_{i,\mathrm{cal}}}{\sigma_{i,\exp}}\right)\right| \tag{6}$$

As shown as in the Tables 1 and 2, the experimental and calculated the values of $\Delta\sigma_\circ$ are compared. Good agreement in most cases is to be noted. The reported RAD% values in these tables indicate that Eq. (1) can accurately calculate the surface tension of a pure solute from the surface tension of its solution in a solvent with known surface tension. This provides a means for obtaining the surface tension of a

Table 1

Experimental and calculated differences of surface tensions of solvent and solute ($\Delta\sigma_\circ$,Eq. (1)), surface Gibbs energy change ($\Delta G_s/RT$,Eq. (1)), standard Gibbs energy of adsorption ($\Delta G^\circ/RT$, Eq. (5)), molar surface area (A_2, Eq. (3)), excess number of molecular layers δ_2^E, Eq. (2)) and relative absolute deviation percent (RAD%) in calculating the surface tension of pure solute (Eq. (6)), for several ionic liquid–organic binary mixtures, and the references for the experimental data.

Binary mixture	T/K	$\Delta\sigma_{\exp}/(\mathrm{mN\cdot m^{-1}})$	$\Delta\sigma_{\mathrm{cal}}/(\mathrm{mN\cdot m^{-1}})$	$\Delta G_s/RT$	$\Delta G^\circ/RT$	$A_2/(^\circ A_2)$	δ_2^E	RAD%	Ref.
$[C_8Quin][NTF_2](1)$ + hexanol(2)	298.15	6.32	6.91	−0.0010	1.9320	40.7584	−0.1136	0.0533	[31]
	308.15	6.25	7.07	0.0592	2.0080	40.5952	0.0019	0.1104	
	318.15	6.67	7.28	0.0908	2.0759	41.0930	0.0021	0.0669	
$[BMIM][BF_4](1)$ + ethanol(2)	298.15	23.33	24.40	0.6259	3.8205	40.8587	0.0006	0.0557	[32]
$[HMIM][BF_4](1)$ + ethanol(2)	298.15	14.33	15.10	0.2390	2.9537	40.8587	0.0010	0.0425	[32]
$[MOIM][BF_4](1)$ + ethanol(2)	298.15	9.82	10.00	−0.0020	2.3006	40.8587	−0.0823	0.0030	[32]
$[EMIM][CH_3SO_4]$ + methanol(2)	298.15	36.37	36.22	0.0178	3.6075	41.8979	0.0343	0.0007	[33]
$[EMIM][CH_3SO_4]$ + ethanol(2)	298.15	30.62	30.46	0.6109	4.0273	40.8587	0.0008	0.0053	[33]
$[MMIM][CH_3SO_4](1)$ + ethanol(2)	298.15	34.91	37.25	1.5412	5.1588	53.2370	0.0005	0.1718	[34]
$[EMIM][NO_3](1)$ + methanol(2)	298.15	35.95	36.40	−0.6463	2.9483	41.8979	−0.0010	0.0426	[35]
$[EMIM][NO_3](1)$ + ethanol(2)	298.15	35.75	35.76	0.4700	4.0468	37.4515	0.0011	0.0000	[35]
$[C_4MIM][NTF_2](1)$ + 1-propanol(2)	298.15	9.46	9.80	−0.1244	2.1580	41.9837	−0.0013	0.0212	[36]
$[EMIM][CH_3SO_4](1)$ + 1-butanol(2)	298.15	29.00	28.04	2.3495	5.6831	47.3571	0.0002	0.1652	[34]
$[MMIM][CH_3SO_4](1)$ + 1-butanol(2)	298.15	32.79	35.95	2.5120	6.0942	46.3751	0.0003	0.3133	[34]
$[EMIM][NTF_2](1)$ + THF(2)	293.15	8.83	8.87	−0.4005	1.7822	54.9267	−0.0005	0.0002	[37]
	298.15	9.22	9.42	1.8213	4.0642	54.6079	0.0001	0.0056	
	303.15	9.52	9.51	−0.5108	1.7415	54.3859	0.0000	0.0000	
	308.15	9.97	10.04	−0.5447	1.7618	54.2384	0.0000	0.0008	
$[EMIM][NTF_2](1)$ + acetonitrile (2)	293.15	7.19	7.18	−1.5606	0.4107	50.4649	−0.0001	0.0000	[37]
	298.15	7.53	7.55	−1.5141	0.5074	50.1624	−0.0001	0.0000	
	303.15	7.90	7.90	−1.5051	0.5618	49.9659	−0.0001	0.0000	
	303.00	8.53	8.48	−1.3704	0.7673	49.7476	−0.0001	0.0003	
	313.15	8.67	8.70	−1.4482	0.7152	49.4901	−0.0001	0.0012	
$[C_6H_{13}OCH_2MIM][BF_4](1)$ + methanol(2)	308.18	0.04	1.00	0.7613	−2.4521	41.2103	0.0211	4.3888	
	318.18	0.08	0.01	0.0978	−2.8396	41.3904	0.0539	0.1800	[32]
$[C_4MIM][NTF_2](1)$ + 1-butanol(2)	293.15	7.19	6.25	−1.3400	0.5121	122.98	−0.2323	0.1189	[36]
	298.15	8.84	8.20	0.0200	2.1245	64.20	0.3298	5.3222	[38]
$[EMIM][SCN](1)$ + pyridine(2)	298.15	15.6	17.74	0.7701	3.6487	62.11	0.5772	0.3271	[38]
$[EMIM][SCN](1)$ + pyrrole(2)	298.15	11.4	13.62	0.9895	3.6011	55.71	0.3093	0.2946	[38]
$[EMIM][SCN](1)$ + thiophene(2)	298.15	21.40	25.26	1.0647	0.98954	67.73	0.0294	1.0522	[38]