

SOLID-LIQUID EQUILIBRIUM IN THE SYSTEMS WITH AN IONIC LIQUID

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An active interest in ionic liquids has grown over the last years. This relatively new class of solvents appears to be potentially useful as a “greener” alternative to volatile organic compounds. This work was aimed at studying the effect of addition of the ionic liquid 1-butyl-3-methylimidazolium chloride to two systems (acetic acid (1)–formamide (2) and propionic acid (1)–formamide (2)) on formation of a compound in the solid phase. In previous work, the presence of a solid compound with a formula $(\text{CH}_3\text{COOH})_2\cdot\text{HCONH}_2$ was investigated in the binary system acetic acid (1)–formamide (2) and a stable solid compound with a different formula $\text{CH}_3\text{CH}_2\text{COOH}\cdot(\text{HCONH}_2)_2$ was found in the binary system propionic acid (1)–formamide (2). In both cases the compound formation is attributed to a strong cross-association (O...H...N). Solid-liquid equilibrium of the systems measured in this work was determined from time-temperature warming curves. In both measured ternary systems with a small addition of the ionic liquid 1-butyl-3-methylimidazolium chloride (i.e. the systems acetic acid (1)–formamide (2)–1-butyl-3-methylimidazolium chloride (3) and propionic acid (1)–formamide (2)–1-butyl-3-methylimidazolium chloride (3)) the above mentioned stable solid compounds are formed and the corresponding melting temperature of these compounds decreased. Dissociation parameters were modelled thermodynamically for solid adducts.

Keywords: Experimental data; Acetic acid; Formamide; Propionic acid; Solid-liquid equilibrium; 1-Butyl-3-methylimidazolium chloride.

In our preceding studies of solid-liquid equilibrium several solid adducts have been identified. These solid compounds were stable in the solid phase but unstable in the liquid phase. We were interested in the stability of the compounds. In the recently studied ternary system acetic acid–propionic acid–formamide¹ both expected stable adducts were found. It was found² that 1-butyl-3-methylimidazolium chloride yields different crystalline polymorphs from different solutions and the melt can thus inhibit crystalliza-

tion. The present study investigates the possible formation of adducts in presence of ionic liquid. Moreover dissociation quantities were calculated for the region of solid compounds.

EXPERIMENTAL

Chemicals

All chemicals used were supplied by Fluka: acetic acid >99.8%, propionic acid >99.5%, formamide >99.5% and 1-butyl-3-methylimidazolium chloride >95.0%. Purity of these substances was tested by determining of their melting points (Table I). They are in a good agreement with the values tabulated by Riddick et al.³ and by Domanska and Mazurowska⁴.

Methods and Measurements

The freezing and melting point apparatus consisted of a cylindrical vessel (30 cm³) placed in a Proline clear-view thermostat on a submersible stirrer, Pt-thermometer recording temperature in the vessel, a multimeter Agilent 34401A, and a computer. Mixing and processes related to the experiment were checked visually through the thermostat window. The resistance thermometer used is ITS-90 certified and the calibration was checked at the triple point of water. The rime on the thermometer which made homogenization of a mixture more difficult was reduced by placing the thermometer into a narrow glass tube filled with ethanol.

Similarly to previous work⁵, warming curves were used to read the liquidus temperatures of measured mixtures with known composition. The rate of temperature change was 2 K h⁻¹. Temperature changes were observed on a PC monitor using an HP-VEE program. More than 100 000 values of temperature (resistance) were often collected in one run; temperature was recorded every 2 s. Generally, the determination of temperature was reproducible within 0.15 K in consecutive experiments.

Solvent mixtures were prepared on mass basis, so that composition could be calculated with the accuracy ± 0.0001 of mole fraction. Stock solutions of an ionic liquid with the acid were prepared in both cases. Ternary mixtures were prepared by adding formamide (2) to a weighed amount of the stock solution.

TABLE I
Melting temperatures of pure compounds

Compound	$T_{\text{fus}}(\text{exp})$, K	$T_{\text{fus}}(\text{lit})$, K	Ref.
Acetic acid	289.84	289.81	3
Formamide	275.54	275.70	3
Propionic acid	252.54	252.45	3
1-Butyl-3-methylimidazolium chloride	341.90	341.94	4

Compositions of the stock solutions were $x_1 = 0.9$ and $x_3 = 0.1$ for the mixture of acetic acid (1) and 1-butyl-3-methylimidazolium chloride (3), and $x_1 = 0.8991$ and $x_3 = 0.1009$ for the mixture of propionic acid (1) and 1-butyl-3-methylimidazolium chloride (3). The stock solutions were kept under dry nitrogen and over 4 Å molecular sieves. The stock bottles were sealed with Parafilm™ to prevent the access of air humidity.

RESULTS AND DISCUSSION

In our previous works^{6,7} the existence of adducts with a congruent melting point in mixtures of formamide with acetic or propionic acid has been reported. In the acetic acid-formamide system a 2:1 adduct $(\text{CH}_3\text{COOH})_2 \cdot \text{HCONH}_2$ was found in the solid phase, whereas in the propionic acid-formamide system stable 1:2 $\text{CH}_3\text{CH}_2\text{COOH} \cdot (\text{HCONH}_2)_2$ and metastable 1:1 $\text{CH}_3\text{CH}_2\text{COOH} \cdot \text{HCONH}_2$ adducts were formed in the solid phase. Table II shows the melting points of compounds as determined by the dystectic points on the binary solid-liquid equilibrium curves.

After an addition of a substance into a pure compound the melting temperature of the pure compound decreases. Similarly, melting temperature of a mixture usually decreases after an addition of a substance into the mixture as can be seen in some phase diagrams of organic systems⁸. The melting temperatures of solid adducts in this work decreased as it was expected after a small addition of the ionic liquid 1-butyl-3-methylimidazolium chloride into systems consisting of a carboxylic acid (i.e. acetic acid or propionic acid) and formamide (see Table II). In the ternary system acetic acid (1)-formamide (2)-1-butyl-3-methylimidazolium chloride (3), the melting temperature of formed solid adduct decreased by more than 5 K in comparison with previously measured system acetic acid (1)-formamide (2)⁶.

TABLE II
Melting temperatures of solid adducts in previously studied binary systems and recently studied ternary systems

Adduct	T_{fus} , K in binary system	T_{fus} , K in ternary system
$(\text{CH}_3\text{COOH})_2 \cdot \text{HCONH}_2$	263.95 ^a	255.50 ^c
$\text{CH}_3\text{CH}_2\text{COOH} \cdot (\text{HCONH}_2)_2$	261.25 ^b	255.80 ^d
$\text{CH}_3\text{CH}_2\text{COOH} \cdot \text{HCONH}_2$	233.35 ^b	–

^a System acetic acid (1)-formamide (2)⁶; ^b system propionic acid (1)-formamide (2)⁷; ^c system acetic acid (1)-formamide (2)-1-butyl-3-methylimidazolium chloride (3); ^d system propionic acid (1)-formamide (2)-1-butyl-3-methylimidazolium chloride (3).

In the ternary system propionic acid (1)–formamide (2)–1-butyl-3-methylimidazolium chloride (3) the melting temperature of formed solid adduct decreased by more than 8 K in comparison with previously measured system propionic acid (1)–formamide (2)⁷.

All experimental points obtained for the acetic acid (1)–formamide (2)–1-butyl-3-methylimidazolium chloride (3) system are given in Table III and plotted in Fig. 1 (x_2 denotes mole fraction of formamide in a mixture), experimental points obtained for the propionic acid (1)–formamide (2)–1-butyl-3-methylimidazolium chloride (3) system are given in Table IV and plotted in Fig. 2. It is apparent that both stable adducts again appear in both the measured systems.

TABLE III

Solid-liquid equilibria in the acetic acid (1)–formamide (2)–1-butyl-3-methylimidazolium chloride (3) system ($x_1:x_3 = 9:1$)

x_2	0.0000	0.1055	0.1968	0.3003	0.3003	0.3491
T , K	281.09	275.74	269.58	255.56	261.77	255.36
x_2	0.3491	0.4003	0.4459	0.4981	0.5501	
T , K	258.52	254.81	253.41	249.56	242.41	

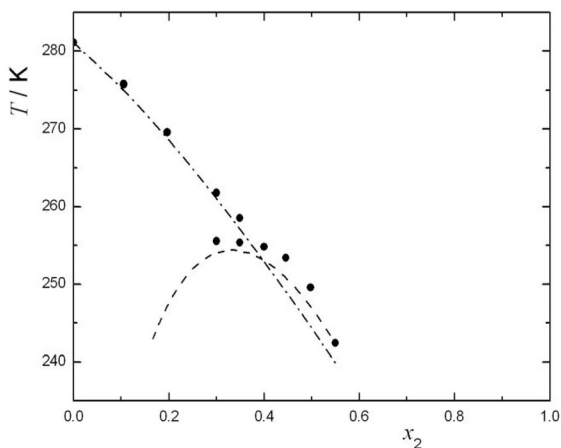


FIG. 1

Solid-liquid equilibria in the acetic acid (1)–formamide (2)–1-butyl-3-methylimidazolium chloride (3) system ($x_1:x_3 = 9:1$): ●, experimental results; dash-and-dotted curve, calculated from Eq. (1); dashed curve, calculated for the adduct region

Solid-liquid equilibrium in the studied mixtures was described thermodynamically. The dash-and-dotted curves in Figs 1 and 2 were calculated from the following equation⁹

$$\ln(\gamma_i x_i) = -\Delta_{\text{fus}} H_{m,i}^{\circ} / R \left(\frac{1}{T} - \frac{1}{T_{\text{fus},i}} \right) \quad (1)$$

derived for systems with no solid solubility and temperature-independent $\Delta_{\text{fus}} H_{m,i}^{\circ}$. In the equation i corresponds to the substance whose crystals are present, x_i is its mole fraction and γ_i activity coefficient in the solution

TABLE IV

Solid-liquid equilibria in the propionic acid (1)-formamide (2)-1-butyl-3-methylimidazolium chloride (3) system ($x_1:x_3 = 8.9108:1$)

x_2	0.4480	0.4480	0.5008	0.5378	0.5564	0.5751	0.5751	0.6000
T , K	244.46	251.27	244.53	244.52	255.78	243.44	255.94	255.64
x_2	0.6245	0.6245	0.7042	0.7167	0.7523	0.8520	1	
T , K	243.37	255.23	250.52	251.82	255.03	263.57	275.54	

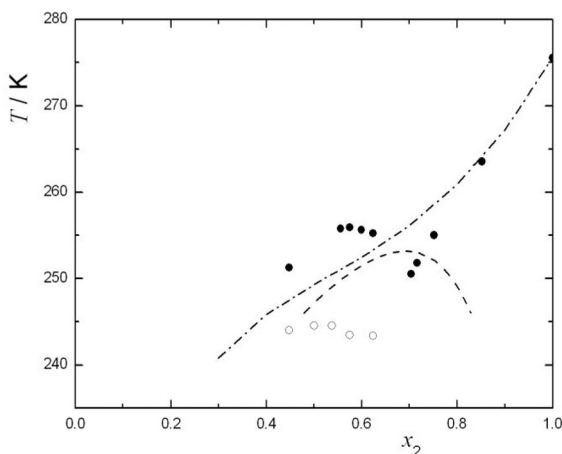


FIG. 2

Solid-liquid equilibria in the propionic acid (1)-formamide (2)-1-butyl-3-methylimidazolium chloride (3) system ($x_1:x_3 = 8.9108:1$): ●, experimental results (liquidus); ○, experimental results (solidus); dash-and-dotted curve, calculated from Eq. (1); dashed curve, calculated for the adduct region

that is in equilibrium with the crystals, $T_{\text{fus},i}$ and $\Delta_{\text{fus}} H_{m,i}^{\circ}$ are its fusion temperature and molar enthalpy of fusion. The curves were calculated with molar enthalpies of fusion $\Delta_{\text{fus}} H_{m,1}^{\circ} = 11\,720 \text{ J mol}^{-1}$ for acetic acid³ and $\Delta_{\text{fus}} H_{m,2}^{\circ} = 6\,690 \text{ J mol}^{-1}$ for formamide³.

Activity coefficients in the ternary systems were modeled by the two-parameter Redlich–Kister equation¹⁰

$$\ln \gamma_1 = b_{12} x_2 (1 - x_1) + b_{13} x_3 (1 - x_1) - b_{23} x_2 x_3 + c_{12} x_2 [x_1 + (x_1 - x_2)(1 - 2x_1)] - 2x_2 x_3 (x_2 - x_3) c_{23} + c_{13} x_3 [x_1 + (x_1 - x_3)(1 - 2x_1)]$$

$$\ln \gamma_2 = b_{12} x_1 (1 - x_2) - b_{13} x_1 x_3 + b_{23} x_3 (1 - x_2) + c_{12} x_1 [-x_2 + (x_1 - x_2)(1 - 2x_1)] - 2x_1 x_3 (x_1 - x_3) c_{13} + c_{23} x_3 [x_2 + (x_2 - x_3)(1 - 2x_2)] \quad (2)$$

$$\ln \gamma_3 = -b_{12} x_1 x_2 + b_{13} x_1 (1 - x_3) + b_{23} x_2 (1 - x_3) - 2c_{12} x_1 x_2 (x_1 - x_2) + c_{13} x_1 [-x_3 + (x_1 - x_3)(1 - 2x_3)] + c_{23} x_2 [-x_3 + (x_2 - x_3)(1 - 2x_3)]$$

with parameters fitted from binary data. From the binary data for the acetic acid (1)–formamide (2) system⁶, following parameters were obtained: $b_{12} = -0.0485$ and $c_{12} = -0.224$. For the propionic acid (1)–formamide (2) system⁷, parameters $b_{12} = 1.0522$ and $c_{12} = 0$ were found. Activity coefficients in the binary system propionic acid (1)–formamide (2) were modeled by the Redlich–Kister equation with one parameter because the region of the stable solid adduct takes a big part of the phase diagram, there were not enough activity coefficients for fitting and the two-parameter Redlich–Kister equation is not giving better results.

As parameters b_{13} , b_{23} , c_{13} and c_{23} were not known, simplified relations were used for the calculations:

$$\ln \gamma_1 = b_{12} x_2 (1 - x_1) + c_{12} x_2 [x_1 + (x_1 - x_2)(1 - 2x_1)] \quad (3)$$

$$\ln \gamma_2 = b_{12} x_1 (1 - x_2) + c_{12} x_1 [-x_2 + (x_1 - x_2)(1 - 2x_1)]$$

which are valid either for $x_3 \rightarrow 0$ or in the case of ideal behavior of both binary mixtures of acid (i.e. acetic acid or propionic acid) with 1-butyl-3-methylimidazolium chloride ((1)–(3) and (2)–(3)).

The temperature at which a solid adduct is in equilibrium with the liquid phase was calculated from its equilibrium requirement $\Delta_{\text{diss}}G_1^\circ = -RT \ln (a_{\text{AA}})_{\text{eq}}^2 (a_{\text{F}})_{\text{eq}}$ for the $(\text{CH}_3\text{COOH})_2 \cdot \text{HCONH}_2$ adduct and $\Delta_{\text{diss}}G_{\text{II}}^\circ = -RT \ln (a_{\text{PA}})_{\text{eq}}^2 (a_{\text{F}})_{\text{eq}}$ for the adduct $\text{CH}_3\text{CH}_2\text{COOH} \cdot (\text{HCONH}_2)_2$. Here $\Delta_{\text{diss}}G_1^\circ$ is the standard Gibbs energy of the first adduct dissociation $\text{AA}_2\text{F}(\text{s}) = 2 \text{AA}(\text{l}) + \text{F}(\text{l})$ whereas $\Delta_{\text{diss}}G_{\text{II}}^\circ$ is the standard Gibbs energy of the second adduct dissociation $\text{PAF}_2(\text{s}) = \text{PA}(\text{l}) + 2 \text{F}(\text{l})$ where AA stands for acetic acid, PA for propionic acid and F for formamide. To estimate the region with a solid compound knowledge of the temperature dependence for $\Delta_{\text{diss}}G^\circ$ from the relevant binary systems is necessary. Temperature dependences for $\Delta_{\text{diss}}G^\circ$ were obtained from the relevant binary systems as $\Delta_{\text{diss}}G_1^\circ = 12\,289 - 30 T$ for the acetic acid (1)–formamide (2) and $\Delta_{\text{diss}}G_{\text{II}}^\circ = 4\,891 - 11 T$ for the propionic acid (1)–formamide (2) binary systems.

As it is evident from Fig. 1, even a simple model describes the main features of the phase diagram very well for the ternary system acetic acid (1)–formamide (2)–1-butyl-3-methylimidazolium chloride (3). The calculated solubility curve intersects the calculated curve of the solid adduct, which is typical for the formation of a stable compound. This corresponds with the present experimental data.

As it is evident from Fig. 2, even a simple model describes the main features of the phase diagrams very well although the calculated small temperature difference between the calculated solubility curve and the calculated curve for the solid adduct region would yield metastable adducts in the ternary system propionic acid (1)–formamide (2)–1-butyl-3-methylimidazolium chloride (3).

The estimates of the solid adducts region in the ternary systems after the addition of the ionic liquid from binary data give slightly lower temperature values than experimental data. The corresponding comparison of the estimate with experiment is qualitatively better for the ternary system acetic acid (1)–formamide (2)–1-butyl-3-methylimidazolium chloride (3) than for the ternary system propionic acid (1)–formamide (2)–1-butyl-3-methylimidazolium chloride (3).

CONCLUSIONS

In previous works, adducts which are stable in the solid phase were identified in the systems acetic acid (1)–formamide (2)⁶, propionic acid (1)–

formamide (2)⁷ and acetic acid (1)–propionic acid (2)–formamide (3)¹. The solid adduct formed of two molecules of acetic acid and one molecule of formamide was identified in the system acetic acid (1)–formamide (2), and in the system propionic acid (1)–formamide (2), the stable adduct formed of one molecule of propionic acid and two molecules of formamide was found. Both the above-mentioned adducts are formed in the ternary system acetic acid (1)–propionic acid (2)–formamide (3) as well.

Results obtained in this work have shown that solid adducts formed in the system of formamide and acetic or propionic are stable also in the presence of 1-butyl-3-methylimidazolium chloride (i.e., in the systems acetic acid (1)–formamide (2)–1-butyl-3-methylimidazolium chloride (3) and propionic acid (1)–formamide (2)–1-butyl-3-methylimidazolium chloride (3)).

The estimate for the region of the solid adduct in the system acetic acid (1)–formamide (2)–1-butyl-3-methylimidazolium chloride (3) is in good agreement with experimental data.

The stable adduct formed in the ternary system propionic acid (1)–formamide (2)–1-butyl-3-methylimidazolium chloride (3) was found to be stable in the solid phase which is in contradiction with model predictions that assume the metastable formation of a metastable adduct in the system propionic acid (1)–formamide (2)–1-butyl-3-methylimidazolium chloride (3).

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REFERENCES

1. Sedláková Z., Malijejská I.: *Fluid Phase Equilib.* **2007**, *261*, 129.
2. Holbrey J. D., Reichert W. M., Nieuwenhuyzen M., Johnson S., Seddon K. R., Rogers R. D.: *Chem. Commun.* **2003**, 1636.
3. Riddick J. A., Bunger W. B., Sakano T. K.: *Organic Solvents*, Vol. II, pp. 251, 253 and 444. Wiley, New York 1986.
4. Domanska U., Mazurowska L.: *Fluid Phase Equilib.* **2004**, *221*, 73.
5. Abrman P., Malijejská I.: *Fluid Phase Equilib.* **1999**, *166*, 47.
6. Malijejská I., Sedláková Z.: *J. Mol. Liq.* **2006**, *125*, 72.
7. Sedláková Z., Malijejská I., Bureš M.: *Collect. Czech. Chem. Commun.* **2007**, *72*, 899.
8. Matsuoka M., Garside J., Davey R. J., Jones A.: *Advances in Industrial Crystallization*, pp. 224–229. Butterworth–Heinemann, Oxford 1991.
9. Prausnitz J. M., Lichtenthaler R. N., de Azevedo E. G.: *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed., p. 641. Prentice–Hall, New Jersey 1999; ISBN 0-13-977745-8.
10. Novák J. P., Matouš J., Pick J.: *Liquid–Liquid Equilibria*, p. 291. Academia, Prague 1987.