Thermodynamic properties of 1-butanol + butylamines

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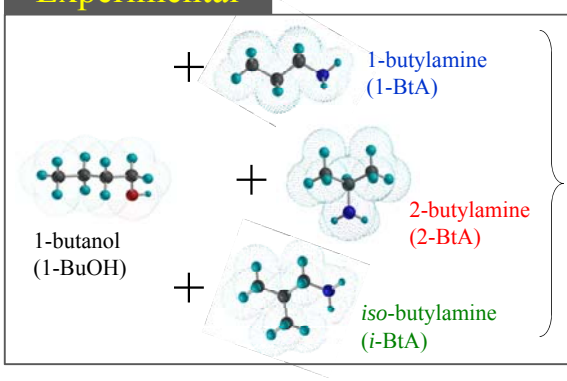
Introduction

Mixtures of alcohols + amines showed a characteristic concentration-dependence of glass transition temperature, viscosity and were large exothermic reaction on mixing. However most of those have been studied in liquid phase, and there are few report in solid-liquid equilibrium. But solidus and liquidus properties were not compared by means of molecular interactions of alcohols + amines.

To clarify the steric effect and hydrogen bond state on 1-butanol and butylamine isomer mixtures, and phase diagram of glass transition and melting of solidus line were compared with excess enthalpies and quantum chemical results.

Experimental



①DSC

Hitachi High-Tech
DSC7000X
High Sensitivity Differential Scanning Calorimeter

⇒Glass transition and melting temperature

②Microcalorimetry

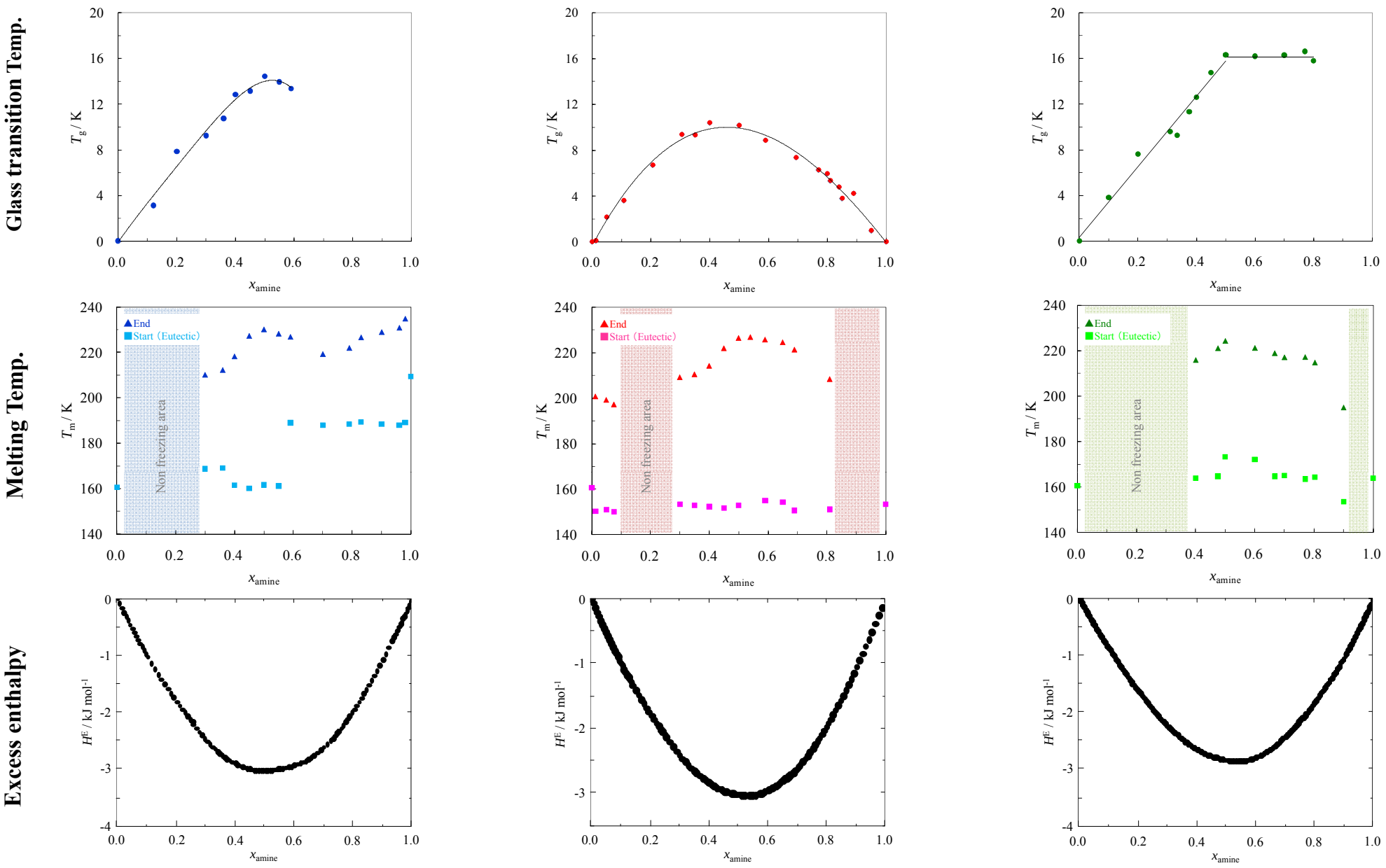
⇒Excess enthalpy of mixing

③MO method

⇒Molecular interaction energy

Results and Discussions

■Comparison T_g and T_m with excess enthalpy H^E



■Correlation between formation enthalpy $\Delta_f H$ and entropy $T\Delta_f S$

$$H^E / \text{J mol}^{-1} = (1 - x)x \sum_{i=1}^{k} A_i (1 - 2x)^{i-1} \quad \cdots (1)$$

$$s_f / \text{Jmol}^{-1} = \left[\sum_{i=1}^{n} \{H^E(\text{obs.}) - H^E(\text{calc.})\}^2 / (n - k) \right]^{1/2} \quad \cdots (2)$$

Table 1 An example of best-fit values for the coefficients A_i of Eqn. (1) and the calculated standard deviations of the fit s_f.

System	A_1	A_2	A_3	A_4	A_5	s_f / J mol^{-1}
1-BuOH + *i*-BtA	-11391	1195.6	2142.9	-241.6	-1445.8	7.04

System	$H^{E,\infty}_{\text{alcohol}}$ / kJ mol^{-1}	$H^{E,\infty}_{\text{amine}}$ / kJ mol^{-1}
1-BuOH + *i*-BtA	-9.7	-13.2

Table 2 Thermodynamic quantities for 1:1 complex formation of 1-butanol + butylamines, **Rich amines**.

System	K	$\Delta_f G$ / kJ mol^{-1}	$\Delta_f H$ / kJ mol^{-1}	$T\Delta_f S$ / kJ mol^{-1}
(1-*x*)1-BuOH + *x*1-BtA	0.892	-0.284	-11.39	-11.11
(1-*x*)1-BuOH + *x*2-BtA	1.064	0.154	-11.39	-11.54
(1-*x*)1-BuOH + *x*i-BtA	1.003	0.007	-13.02	-13.03

Table 3 Thermodynamic quantities for 1:1 complex formation of 1-butanol + butylamines.

System	K	$\Delta_f G$ / kJ mol^{-1}	$\Delta_f H$ / kJ mol^{-1}	$T\Delta_f S$ / kJ mol^{-1}
(1-*x*)1-BuOH + *x*1-BtA	0.884	-0.306	-10.52	-10.21
(1-*x*)1-BuOH + *x*2-BtA	0.866	-0.356	-10.85	-10.49
(1-*x*)1-BuOH + *x*i-BtA	1.028	0.068	-9.679	-9.746

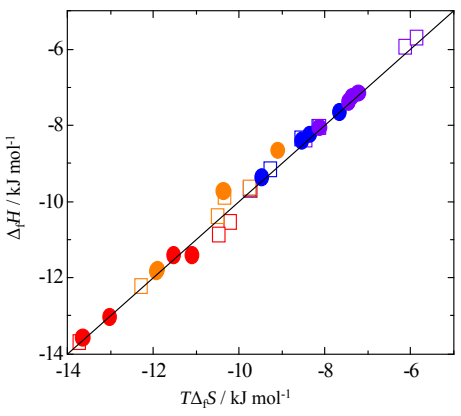


Fig. 1 Correlation between molar enthalpies and molar entropies of formation of butanol isomers + butylamine isomers: ●, rich amine; □, rich alcohol;
●, 1-butanol + 1, 2, *i*, *t*-butylamine; ●, 2-butanol + 1, 2, *i*, *t*-butylamine;
●, *i*-butanol + 1, 2, *i*, *t*-butylamine; ●, *t*-butanol + 1, 2, *i*, *t*-butylamine;
□, 1-butanol + 1, 2, *i*, *t*-butylamine; □, 2-butanol + 1, 2, *i*, *t*-butylamine;
□, *i*-butanol + 1, 2, *i*, *t*-butylamine; □, *t*-butanol + 1, 2, *i*, *t*-butylamine

■ Quantum chemical results of 1:1 interaction

Table 4 Interaction energies and hydrogen bond energies of 1-butanol+butylamines

System	E1	E2	E3	Interaction energy	N: H-O
	hartree	hartree	hartree	kJ mol^{-1}	kJ mol^{-1}
1-BtOH + 1-BtA	-444.37916	-212.27178	-232.09999	-19.4	94.3
1-BtOH + 2-BtA	-444.38352	-232.10059	-212.27418	-23	102.3
1-BtOH + *i*-BtA	-444.38067	-232.10061	-212.27206	-21	84.9

Table 5 Interaction of 1-butanol + butylamines in kJ mol^{-1}

System	Electrostatic energy (PL state, incl. EPLs)	Exchange repulsion energy (PL state)	Charge transfer energy (PL state)	Dispersion force (PL state)	Total interaction (PL state)
1-BtOH + 1-BtA	-90.83	82.26	-25.86	-31.88	-66.3
1-BtOH + 2-BtA	-96.99	86.25	-29.23	-28.49	-68.45
1-BtOH + *i*-BtA	-83.39	71.66	-24.75	-24.1	-60.59

Conclusions

- The results of glass transition and melting temperature were in good agreement with excess enthalpy of mixing. Both results indicated the most stable composition in solid and liquid phase were equimolar composition.
- The concentration dependence of glass transition temperature on 1-butanol + *i*-butylamine mixtures showed unique behaviors than other systems.
- Excess enthalpies of mixing of 1-butanol and butylamines were large exothermic over the whole range of mole fractions. The most stable composition of mixture were around equimolar composition.
- Thermodynamic properties of 1:1 complex were determined. Enthalpy and entropy of formation of 1-butanol + butrylamines were shown linear relation.

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