

ISOBARIC MOLAR HEAT CAPACITY AND MELTING PARAMETERS OF 1-ETHYL- AND 1-BUTHYL-3-METHYLIMIDAZOLIUM METHANESULFONATES

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Imidazolinium ionic liquids containing methanesulfonate ions are commercially demanded along with ionic liquids containing classical anions such as chlorine, bromine, and acetate [1]. This is since the production of methanesulfonic acid has recently increased by applying one-stage synthesis method with a high yield [2]. It should also be emphasized that methanesulfonates is biodegradable [3], and ionic liquids attract are of interest to scientists and technologists due to unique properties, such as low vapor pressure, high thermal stability, and capability to recovery in solvent possesses. The objects of the present study are two ionic liquids 1-ethyl- and 1-buthyl-3-methylimidazolium methanesulfonates ($[\text{C}_2\text{mim}][\text{SO}_3\text{CH}_3]$ and $[\text{C}_4\text{mim}][\text{SO}_3\text{CH}_3]$, respectively).

Information on thermodynamic properties of these ionic liquids is fragmentary presented in literature. It is known enthalpies of formation of these substances in the liquid and gaseous state [4]. However, $[\text{C}_2\text{mim}][\text{SO}_3\text{CH}_3]$ and $[\text{C}_4\text{mim}][\text{SO}_3\text{CH}_3]$ are solid at the room temperature. To recalculate the thermodynamic functions of formation from liquid to the solid state, it is necessary to know the melting points, heats of fusion, and the isobaric heat capacity of solid and liquid phases of the compounds. There are data on the isobaric heat capacity of liquid $[\text{C}_2\text{mim}][\text{SO}_3\text{CH}_3]$ [5], ones for solid phase and for another ionic liquid $[\text{C}_4\text{mim}][\text{SO}_3\text{CH}_3]$ are absent. As to fusion parameters, there is only melting point of $[\text{C}_4\text{mim}][\text{SO}_3\text{CH}_3]$ [6].

The aim of the present work is devoted to determination following thermodynamic properties of $[\text{C}_2\text{mim}][\text{SO}_3\text{CH}_3]$ and $[\text{C}_4\text{mim}][\text{SO}_3\text{CH}_3]$: melting points, heat of fusions and isobaric heat capacity of solid phases. For these purpose DSC 204 F1 Phoenix (NETZSCH GmbH) was applied. Sample purities and fusion parameters were obtained by ASTM E928 at the heating rate $0.5 \text{ K}\cdot\text{min}^{-1}$. Melting points were corrected to zero contamination by Schroeder's law (Table). Isobaric heat capacity was measured by ASTM E1269 at the heating rate $10 \text{ K}\cdot\text{min}^{-1}$ in the temperature range from 150 K to the melting point of corresponding substance.

Table. Source, purity and melting parameters of $[\text{C}_2\text{mim}][\text{SO}_3\text{CH}_3]$ and $[\text{C}_4\text{mim}][\text{SO}_3\text{CH}_3]$.

Formula	Source	Purity/ mol. %	T_m/K	$\Delta_m H^0(T_m)/\text{kJ}\cdot\text{mol}^{-1}$
$[\text{C}_2\text{mim}][\text{SO}_3\text{CH}_3]$	«Roth»	99.14±0.03	313.4±0.2	15.3±1.1
$[\text{C}_4\text{mim}][\text{SO}_3\text{CH}_3]$	«Alfa Aesar»	99.52±0.03	349.1±0.2	25.2±1.8

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[1] https://chemicals.basf.com/global/en/Intermediates/Product_groups/Ionic_liquids.html

[2] C. Diaz-Urrutia, T. Ott, *Science*, 2019, 363, 1329.

[3] M.D. Gernon, *Green Chemistry*, 1999, 1, 127.

[4] D.H. Zaitsau, A.V. Yermalayeu, A.A. Pimerzin, S.P. Verevkin, *Chemical Engineering Research and Design*, 2018, 137, 164.

[5] M. Musial, M. Zorebski, M. Dzida, J. Safarov, E. Zorebski, E. Hassel, *Journal of Molecular Liquids*, 2019, 276, 885.

[6] N.S.M. Vieira, I.Vazquez-Fernandez, J.M.M. Araujo, N.V. Plechkova, K.R. Seddon, L.P.N. Rebelo, A.B. Pereiro, *Journal of Chemical Engineering Data*, 2019, 64, 4891.