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Osmotic and Activity Coefficients of Lithium and Tetramethylguanidinium Sulfamates at 298.15 K

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Osmotic and activity coefficient data are reported for the lithium and tetramethylguanidinium salts of sulfamic acid. These coefficients are compared with those of the previously reported sodium and potassium salts and with the corresponding salts of methanesulfonic acid.

Osmotic and activity coefficient data have been previously reported (*1*) for sulfamic acid and for its sodium and potassium salts. At that time, the coefficients of the two salts were compared with the coefficients of the corresponding salts of methanesulfonic acid. Since the coefficients of the sulfamate salts were appreciably smaller, it was suggested that there might be linear association of the sulfamate anion, especially if resonance structures of the type $H_2N^+{=}SO_3^{2-}$ are at all important. Coefficients for the two salts being presently reported were measured to obtain further information to enable a better understanding of the sulfamate system.

Method

The sulfamic acid was purchased as the "certified" grade with lot analysis from Fisher Scientific Co. Solutions of this acid were carefully neutralized with solutions of C.P. grade lithium carbonate or the free base tetramethylguanidine and evaporated to dryness over H_2SO_4 in vacuum desiccators. The salts were recrystallized several times from alcohol–water mixtures, again dried over H_2SO_4, and stored under vacuum over P_4O_{10}. The molecular weights of the salts were measured by exchange of known weights of the salts on a sulfonate strong-acid ion-exchange resin and titration of the released hydrogen ion. The salts were not hydrates and the molecular weights agreed with the calculated formula weights within the reproducibility of the titration (about 0.1%).

The isopiestic equilibration of these solutions was performed in the usual manner (*2*). It was established that equilibrium was reached when the concentrations of identical samples were within 0.1% agreement with one sample losing solvent and the other gaining solvent to attain equilibrium.

Table I. Molalities of Isopiestic Solutions

	sulfamate			sulfamate	
NaCl	Li	Me_4Gu^a	NaCl	Li	Me_4Gu^a
0.1963	0.1928	0.1968	2.923	2.881	2.946
0.3925	0.3825	0.3946	3.393	3.376	3.441
0.5872	0.5113	0.5901	3.896	3.907	3.987
0.8875	0.8616	0.8910	4.586	4.651	4.728
1.206	1.170	1.211	5.304	5.455	5.582
1.600	1.550	1.605	5.897	6.147	6.271
1.959	1.907	1.963	5.953	6.228	6.363
2.450	2.293	2.459			

[a] Me_4Gu = tetramethylguanidinium.

Table II. Osmotic and Activity Coefficients of Sulfamate Salts at 298.15 K

	Li		Me_4Gu^a	
m	ϕ	γ	ϕ	γ
0.1	0.944	0.796	0.930	0.775
0.2	0.943	0.764	0.922	0.730
0.3	0.943	0.747	0.918	0.703
0.4	0.944	0.736	0.915	0.685
0.5	0.946	0.729	0.916	0.674
0.6	0.949	0.725	0.918	0.664
0.7	0.953	0.722	0.921	0.658
0.8	0.957	0.720	0.924	0.653
0.9	0.961	0.720	0.928	0.650
1.0	0.966	0.720	0.932	0.648
1.2	0.975	0.723	0.939	0.645
1.4	0.985	0.728	0.947	0.644
1.6	0.994	0.734	0.958	0.647
1.8	1.003	0.741	0.970	0.653
2.0	1.012	0.749	0.981	0.658
2.5	1.035	0.771	1.009	0.677
3.0	1.060	0.788	1.035	0.697
3.5	1.085	0.825	1.061	0.721
4.0	1.112	0.858	1.085	0.745
4.5	1.139	0.895	1.109	0.772
5.0	1.162	0.930	1.132	0.800
5.5	1.185	0.967	1.152	0.827
6.0	1.203	1.003	1.163	0.855

[a] Me_4Gu = tetramethylguanidinium.

Results and Discussion

The primary isopiestic equilibration data are presented in Table I. These data have an accuracy of approximately 0.1%. The osmotic and activity coefficients at rounded concentrations are reported in Table II. Osmotic coefficients were calculated from the equation (*3*)

$$\phi = R\phi_{\text{ref}}$$

and activity coefficients from the relationship

$$\ln \gamma = \ln \gamma_{\text{ref}} + \ln R + 2\int_0^{m_{\text{ref}}} (R - 1)\, \mathrm{d} \ln (m\gamma)_{\text{ref}}^{1/2}$$

where $R = m_{\text{ref}}/m$.

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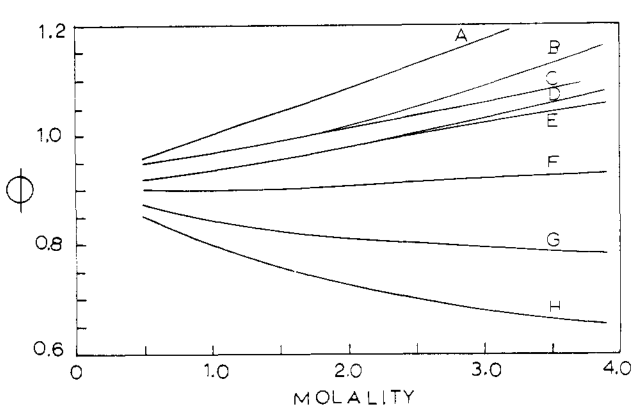

Figure 1. Osmotic coefficients of sulfamate and methanesulfonate salts: (A) lithium methanesulfonate, (B) tetramethylguanidinium methanesulfonate, (C) lithium sulfamate, (D) tetramethylguanidinium sulfamate, (E) sodium methanesulfonate, (F) potassium methanesulfonate, (G) sodium sulfamate, (H) potassium sulfamate. These are plotted from smoothed data.

A comparison of the osmotic coefficients of the sulfamate and methanesulfonate salts is shown graphically in Figure 1. The coefficients of the methanesulfonate salts are larger than those of the corresponding sulfamate salts for all cations. The differences for the lithium and tetramethylguanidinium salts are not as large, however, as for the sodium and potassium salts. It would be expected that the two former cations would ion pair with either anion to a greater extent than the sodium or potassium ion. Any cation ion pairing with the sulfamate anion would be at the expense of the anion ion pairing which has been postulated, and should reduce the difference in the values of the coefficients of the sulfamate and methanesulfonate salts. Alternatively, if the difference in the coefficients is due, in part, to a difference in the solvent structure altering properties of the sulfamate and methanesulfonate anions, the cation-anion pairing should also reduce this effect.

Registry No. Lithium sulfonate, 84849-43-4; tetramethylguanidinium sulfonate, 84849-44-5.

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Thermophysical Properties of Ethylene in the Critical Region

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Thermophysical properties for ethylene were correlated in the critical region of 280.15–284.15 K, 4.5–11.0 mol/dm^3 based on the experimental density measurements of Douslin and Harrison. Extrapolations of the measurements to the critical point (CP) are consistent with modern knowledge of critical-region behavior; the present tables agree with the derived thermodynamic properties of Harrison and Douslin at the above boundaries and, hence, form critical-region companion tables to those of Harrison and Douslin which are further from the CP. In addition to density, enthalpy, and entropy, the isochoric heat capacity is reported in both the homogeneous and heterogeneous regions with sonic velocities also tabulated along the homogeneous side of the saturation envelope.

Ethylene, the leading petrochemical, is frequently pumped across international boundaries and through common carrier pipelines where the volume of the fluid read from flowmeters must be converted to mass from *accurate* knowledge of the density. Metering conditions are often close to the critical point of 282.3502 K (~48.6 °F) and 5.04197 MPa (~730 psia). Discrepancies in the third significant figure of density have led to legal disputes involving millions of dollars per annum in separate cases. The high sensitivity of density to pressure and temperature in the critical region creates problems for single plant inventories as well as the simultaneous use of one pipeline by several firms. The objective of the present work is to provide derived thermophysical properties for ethylene on a fine grid pattern in the immediate critical region.

The present work was completed in 1978; we acknowledge that a number of technical articles concerning ethylene have been published since that time which are uncited and not used in the present correlation.

Critical Constants

The critical temperature was determined by fitting the orthobaric densities of Douslin and Harrison (*1*) to

$$\rho_l - \rho_g = a_1[1 - T/a_2]^{a_3} \qquad (1)$$

where a_2, the critical temperature, was found to be 282.3502 ± 0.0105 K (IPTS - 68), ±0.01 K is attributed to experimental error, and ±0.0005 K is twice the standard deviation of eq 1 to fit the experimental data. The critical density was then found from extrapolation of the rectilinear diameter line to the critical temperature. Finally, the critical pressure was obtained from a nonanalytical vapor pressure equation considered below. The differences between the critical constants selected by Douslin and Harrison and those determined as above were within the precision of the experimental measurements as also noted by Harrison and Douslin (*2*). Thus, the following values of Douslin and Harrison were adopted: T_c = 282.3502 ± 0.0105 K, P_c = 5.04197 ± 0.0026 MPa, and ρ_c = 7.635 ± 0.006 mol/dm^3. For ρ_c, we judge ±0.004 mol/dm^3 to come from experiment and ±0.002 mol/dm^3 from the fitting procedure. For P_c, ±0.0014 MPa is from the fitting procedure whereas ±0.0012 is estimated from experiment. These constants are in good agreement with Moldover's (*3*) visual observations, T_c = 282.344 ± 0.004 K and ρ_c = 7.650 ± 0.021 mol/cm^3, but they are considerably lower than those adopted by Angus et al. (*4*): T_c = 282.65 ± 0.25 K, P_c = 5.076 ± 0.020 MPa, and ρ_c = 7.771 ± 0.071 mol/dm^3. Recently, Hastings et al. (*5*) have selected T_c = 282.3452 ± 0.0017 K, P_c = 5.0403 ± 0.0002

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