Figure 11. Literature comparison of relative volatilities for ethane-ethylene system.

P_r	reference pressure in Goodwin equation
P_R	Raoult's law pressure
P_c	critical pressure
R	gas constant
T	temperature
T_c	critical temperature
V	volume, L/mol
x	liquid mole fraction, unsubscripted means most volatile component
y	vapor mole fraction, unsubscripted means most volatile component
z	overall mole fraction of ethylene in sample cell
Z	vapor compressibility factor
α	relative volatility
δ_{ij}	binary interaction parameter
ρ	density
ϕ_i	fugacity of component i in a mixture

Subscripts

1,2	components in binary system, 1 is most volatile
l	liquid
o	overall
P	constraint on partial derivative to constant pressure
v	vapor
y	constraint on partial derivative to constant composition

Superscripts

l	liquid
v	vapor

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Osmotic and Activity Coefficients of Some Sulfamates and Sulfanilates at 298.15 K

Oscar D. Bonner

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

Osmotic and activity coefficients are reported for solutions of the sodium and potassium salts of sulfamic and sulfanilic acids and for the parent acid. The data are in agreement with the evidence in the literature that sulfamic acid is a moderately strong acid with an ionization constant which is not too different from that of iodic acid.

Moderately strong acids such as iodic or the trihaloacetic acids are a small and unique group in that, while many acids are quite weak or quite strong, there are few acids with ionization constants in the range of 10^{-1}–10. A recent survey article (1) reminded one that sulfamic and sulfanilic acids exist as zwitterions in solution and suggested that a study of the properties of solutions of these acids and their salts might be of interest. The ionization constant for the equilibrium

$$NH_3{}^+SO_3{}^- = NH_2SO_3{}^- + H^+$$
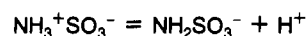
has been reported to be 0.1006 from conductance measure-

Table I. Molalities of Isopiestic Solutions

NaCl	sulfamic acid	sodium sulfa-mate	potassium sulfa-mate	NaCl	sodium sulfa-nilate	potassium sulfa-nilate
0.166_5	0.199_4	0.168_9	0.170_0	0.302_1	0.305_5	0.307_4
0.242_1	0.299_9	0.247_8	0.250_4	0.600_0	0.615_1	0.622_9
0.335_6	0.428_8	0.345_9	0.351_2	0.788	0.813	0.830
0.465_0	0.615_6	0.488_6	0.501_7	1.069	1.125	1.160
0.634	0.866	0.680	0.710	1.263		1.397
0.835	1.171	0.917	0.973	1.336		1.488
1.111	1.608	1.252	1.364	1.584		1.792
1.508	2.267	1.762	1.987	1.859		2.125
1.682		2.003	2.291	2.035		2.335
1.981		2.422	2.829	2.376		2.770
2.117		2.618	3.107	2.666		3.150
2.399		3.026	3.634			
2.716		3.532	4.300			
2.997		4.012	4.966			

Table II. Osmotic Coefficients at 298.15 K

m	sulfamic acid	sodium sulfamate	potassium sulfamate	sodium sulfa-nilate	potassium sulfa-nilate
0.1	0.817	0.924	0.921	0.928	0.927
0.2	0.774	0.908	0.902	0.919	0.915
0.3	0.745	0.896	0.885	0.912	0.906
0.4	0.724	0.884	0.869	0.906	0.899
0.5	0.709	0.874	0.853	0.904	0.894
0.6	0.697	0.867	0.840	0.902	0.889
0.7	0.687	0.860	0.826	0.900	0.886
0.8	0.680	0.854	0.815	0.898	0.882
0.9	0.674	0.848	0.805	0.897	0.877
1.0	0.669	0.843	0.796	0.895	0.871
1.1				0.891	
1.2	0.662	0.836	0.779		0.862
1.4	0.665	0.829	0.764		0.855
1.6	0.650	0.823	0.750		0.851
1.8	0.646	0.817	0.737		0.850
2.0	0.642	0.811	0.725		0.852
2.2	0.638				
2.5		0.802	0.700		0.860
3.0		0.795	0.679		0.867
3.5		0.786	0.667		
4.0		0.780	0.656		
4.3			0.649		

Table III. Activity Coefficients at 298.15 K

m	sulfamic acid	sodium sulfamate	potassium sulfamate	sodium sulfa-nilate	potassium sulfa-nilate
0.1	0.604	0.769	0.761	0.773	0.770
0.2	0.501	0.710	0.701	0.725	0.719
0.3	0.442	0.674	0.660	0.694	0.687
0.4	0.401	0.646	0.627	0.673	0.663
0.5	0.371	0.624	0.599	0.658	0.645
0.6	0.347	0.605	0.575	0.645	0.631
0.7	0.328	0.588	0.552	0.634	0.618
0.8	0.310	0.573	0.533	0.624	0.606
0.9	0.299	0.560	0.516	0.616	0.594
1.0	0.288	0.548	0.501	0.608	0.583
1.1				0.600	
1.2	0.268	0.529	0.474		0.564
1.4	0.253	0.511	0.451		0.548
1.6	0.240	0.496	0.430		0.535
1.8	0.229	0.483	0.412		0.525
2.0	0.220	0.471	0.396		0.518
2.2	0.212				
2.5		0.447	0.362		0.506
3.0		0.428	0.335		0.493
3.5		0.412	0.314		
4.0		0.397	0.298		
4.3			0.288		

ments (*2*) and 0.103 (*3*) from emf measurements. A slight uncertainty exists in these values (*3*) because the extrapolation over a fairly large concentration range is dependent on an arbitrary assumption of ion size.

Method

The sulfamic and sulfanilic acids were purchased as the "certified" grade with lot analysis from Fisher Scientific Co. The sulfamic acid was stored under vacuum over P_2O_5, and the molecular weight by titration agreed with the theoretical weight within the uncertainty of the titration. The dried sample was used without further purification. The sulfanilic acid was the monohydrate, but it was too insoluble for isopiestic studies in any case. Samples of both parent acids were carefully neutralized with NaOH or KOH, and the salts were recrystallized from alcohol–water mixtures.

The isopiestic equilibration of these solutions was performed in the usual manner (*4*). It was established that equilibrium was reached when the concentrations of identical samples were within 0.1% agreement with one sample losing weight and the

Figure 1. Activity coefficients of some sodium salts: (A) sodium methanesulfonate, (B) sodium sulfanilate, (C) sodium *p*-toluenesulfonate, (D) sodium sulfamate.

other gaining weight to attain equilibrium.

Results and Discussion

The primary isopiestic equilibration data are presented in Table I. The osmotic and stoichiometric activity coefficients at rounded concentrations are reported in Tables II and III. Osmotic coefficients were calculated from the equation

$$\phi = (m_{ref}/m)\phi_{ref}$$

and activity coefficients were calculated from the relationship (*5*)

$$\ln \gamma = \ln \gamma_{ref} + \ln \frac{m_{ref}}{m} + 2 \int_0^{m_{ref}} \left(\frac{m_{ref}}{m} - 1\right) d \ln (m\lambda)_{ref}^{1/2}$$

The extrapolation of the molality ratio m(NaCl)/m(sulfamic acid) to infinite dilution was somewhat uncertain because of the greater deviation from unity than would be normal for completely ionized solutes. Data at constant water activities for HIO_3 (*6*) and sulfamic acid solutions were, therefore, used to aid in the extrapolation. The activity coefficient data for sulfamic acid could nevertheless be in error by as much as 1%, but the uncertainty of the osmotic coefficients is the same as
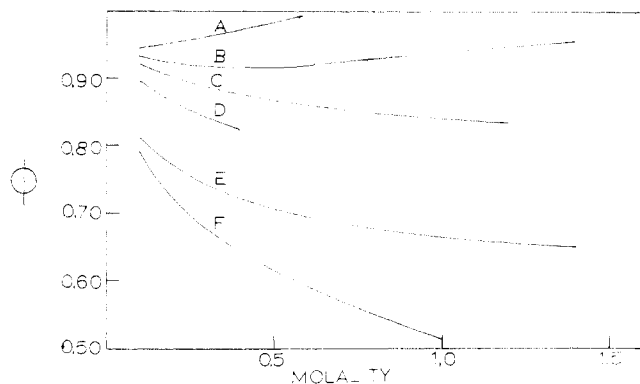
Figure 2. Osmotic coefficients at 25 °C: (A) methanesulfonic acid, (B) sodium methanesulfonate, (C) sodium sulfamate, (D) sodium iodate, (E) sulfamic acid, (F) iodic acid.

that of the salts (about 0.1%).

Stoichiometric activity coefficient data are plotted in Figure 1 for the sodium salts of methanesulfonic, sulfamic, p-toluenesulfonic, and sulfanilic acids, and the behavior is rather unexpected. The methanesulfonate curve lies far above the sulfamate curve. This is not surprising when one realizes that the replacement of the CH_3 group by a NH_2 group permits the linear association of the sulfamate anions especially if resonance structures of the type $H_2N^+ = SO_3^{2-}$ are at all important. The surprising relationship is that between the aromatic compounds where the sulfanilate curve lies above the p-toluenesulfonate curve. Similar relationships also hold true for the potassium salts of these acids.

The order of osmotic coefficients for a strong acid and its salts at any concentration is $H^+ > Li^+ > Na^+ > K^+$, an order due primarily to the differing degrees of hydration of the cations. Incomplete ionization causes the coefficient of an acid to be smaller than that of its salts. The ratio of the coefficients of an acid and its sodium salt at any concentration gives a rough idea of the degree of ionization since the solvation effect of the anion is largely compensated, especially in the case of fairly large anions (6). The coefficients of the sulfamates and iodates of Figure 2 suggest that the ionization constants of the two acids are probably not too different with sulfamic acid being a slightly stronger acid than iodic acid rather than a slightly weaker acid as was calculated from emf and conductance measurements. Methanesulfonic acid, which contains the CH_3 rather than the NH_2 group, is a strong acid, as is shown by the coefficients of the acid and the sodium salt (7, 8).

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Equilibrium Distribution Coefficients of Lead, Copper, and Cadmium in Tin

Yoshio Hoshino* and Taizo Utsunomiya

Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama, Japan 227

The equilibrium distribution coefficients of lead, copper, and cadmium in tin were obtained by using a modified zone refiner. This refiner is characterized by alternating high-speed clockwise and anticlockwise rotations (0–3000 rpm) of the containing tube at short intervals (0.5–10 s) resulting in a thin diffusion layer thickness. The equilibrium distribution coefficients k_0 of these impurities in tin were 0.14 (Pb), 2.0 × 10⁻² (Cu), and 0.48 (Cd), and these values showed good correspondence to those estimated from the phase diagram.

It is important to know the distribution coefficient of a solute in planning a zone refining experiment or process. The methods of determining the equilibrium distribution coefficient are generally classified into three groups: (a) use of a phase diagram, (b) a thermodynamic method based on the laws of dilute solution, and (c) calculation from an effective distribution coefficient obtained by experiment (1). In method a, it is inevitable that the phase equilibrium in a desired binary system near the end composition should be accurately and clearly known. An accurate phase diagram, however, is not available at the desired concentration, especially for very dilute solutions. In method b, solutions would be assumed to be ideal solutions.

In general, however, solutions are not ideal enough to permit more than a rough estimate of the equilibrium distribution coefficient. Therefore, in the present paper, the equilibrium distribution coefficient was obtained by method c, and these values were compared with those estimated from phase diagrams.

According to Burton et al. (2), if the zone travel rate is constant and the diffusion of the impurity in the solid is negligible, the effective distribution coefficient can be expressed by eq 1. By rearranging eq 1, one obtains eq 2a and 2b.

$$k_0/k = k_0 + (1 - k_0)\exp[-f\delta/D] \tag{1}$$

$$\ln(1/k - 1) = \ln(1/k_0 - 1) - f\delta/D \quad \text{for } k < 1 \tag{2a}$$

$$\ln(1 - 1/k) = \ln(1 - 1/k_0) - f\delta/D \quad \text{for } k > 1 \tag{2b}$$

Therefore, by measuring the effective distribution coefficient in the material refined at different zone travel rates with identical stirring conditions, one can obtain the value of the equilibrium distribution coefficient from the intercept of the line plotting ln (1/k - 1) or ln (1 - 1/k) against the zone travel rate.

The zone refining apparatus used in this work is especially intended to make the diffusion layer thickness a minimum and has a characteristic of high-speed clockwise and anticlockwise