example, 1,2,4-trimethylbenzene is given by

$$\Delta \bar{H}^{\infty}{}_{\mathrm{soln}} = \Delta H_{\mathrm{Ph}} + 3\Delta H_{\mathrm{CH_3}} + (\Delta h_{p\text{-CH}_3} + \Delta h_{o\text{-CH}_3}) + (\Delta h_{m\text{-CH}_3} + \Delta h_{o\text{-CH}_3}) + (\Delta h_{p\text{-CH}_3} + \Delta h_{m\text{-CH}_3})$$

By means of the method of least squares, these five parameters ΔH_{Ph}, $\Delta H_{\mathrm{CH_3}}$, $\Delta h_{p\text{-CH}_3}$, $\Delta h_{m\text{-CH}_3}$, and $\Delta h_{o\text{-CH}_3}$ are determined with little standard deviations from the data of the partial molar enthalpy of solution. The parameters are efficient in the systems of long chain *n*-alkane solvents at infinite dilution. The values of parameters are given in Table IV. The predicted value of the enthalpy of solution can be determined through eq 10′. The calculated values are given in Table III. Equation 10′ provides very good agreement between experimental and calculated enthalpy of solution.

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Some Physicochemical Properties of Binary and Ternary Solutions of Sodium Nitrate, Ammonium Nitrate, Propylene Glycol, and Water at 25 °C

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Densities (*d*), relative viscosities (η/η_0), and surface tensions (γ) are reported for some binary and ternary solutions at 25 °C as follows: $NaNO_3$–propylene glycol (PG), *d* to saturation; NH_4NO_3–PG, *d* to saturation; $NaNO_3$–NH_4NO_3–H_2O, *d*, η/η_0, and γ near saturation; $NaNO_3$–NH_4NO_3–PG, *d* and η/η_0 near saturation; $NaNO_3$–H_2O–PG, *d*, γ, and η/η_0 at saturation; NH_4NO_3–H_2O–PG, *d*, η/η_0, and γ at saturation.

Foams in concentrated salt solutions, using water and mixed water/organic solvents, are becoming increasingly important in practical applications. Emphasis is therefore needed on specifying the effectiveness of surfactants in such complex media. As a prerequisite to a study of surfactant effectiveness in these media (to be reported elsewhere), we wished to determine those physicochemical solution properties which might be expected to correlate with the foaming properties of selected surfactants. Density, viscosity, and surface tension were taken to be of primary interest. The components chosen for binary and ternary solutions were relevant to applied interests; they were $NaNO_3$, NH_4NO_3, water, and propylene glycol (PG). Literature data for the desired properties are only partial and in many instances nonexistent. Accordingly in this paper we report results obtained to complement available information.

Experimental Section

$NaNO_3$ and NH_4NO_3 were Anachemia reagent grade, and were used without further purification. The solvents were PG (bp 186–187 °C, Anachemia) and distilled water. If solutions were not already clear they were filtered through paper.

Solution densities were measured by a digital densimeter Model DMA 10 (Anton Paar K.G.) which was calibrated with air and distilled water at 25 °C. Temperature was controlled by a Haake constant temperature circulator Model FS, at 25 ± 0.01 °C. The uncertainty in measured density was about $\pm 2 \times 10^{-4}$ g mL^{-1}.

Solution viscosities were measured with Cannon-Fenske viscometers in a water bath at 25 ± 0.01 °C. Flow times were reproducible to about 0.1 s, and were always greater than 100 s. No correction for kinetic effects was applied. The flow times of salt solutions were determined relative to those for the solvent in the same viscometer in each case, i.e., pure H_2O or pure PG or a mixed H_2O/PG solvent. The precision in relative viscosity η/η_0 was ±0.5%.

The surface tensions of solutions were measured by the drop-weight technique, using a relatively simple apparatus, similar to that described by Patton (*7*). A standardized experimental procedure was adopted for all measurements. The rate of drop formation was controlled by a needle-valve and was maintained between 50 and 60 s. The test liquid was kept at 25

Table I. Densities of Saturated and Unsaturated Solutions of $NaNO_3$–PG and NH_4NO_3–PG at 25 °C

(I) $NaNO_3$–PG

	Composition, g of $NaNO_3$ per 100 g of PG					
0	1.0	1.5	3	5	6	6.65[a]
d 1.0342	1.0452	1.0486	1.0538	1.0639	1.0690	1.0724

(II) NH_4NO_3–PG

	Composition, g of NH_4NO_3 per 100 g of PG					
0	3	5	10	15	20	21.7[a]
d 1.0342	1.0494	1.0538	1.0705	1.0845	1.0971	1.1040

[a] Saturated solution.

Table II. Densities, Relative Viscosities,[a] and Surface Tensions of Solutions Near Saturation in the System $NaNO_3$–NH_4NO_3–H_2O at 25 °C

	Comp wt %					
Solution no.	$NaNO_3$	NH_4NO_3	H_2O	*d*	η/η_0	γ
1	46.0	0	54.0	1.3702	2.79	83.5
2	40.0	10.0	50.0	1.3719	2.71	82.5
3	35.0	20.0	45.0	1.3852	2.86	81.2
4	30.0	30.0	40.0	1.3959	2.99	82.3
5	25.0	45.0	30.0	1.4352	4.07	84.5
6	20.0	50.0	30.0	1.4179	3.77	83.8
7	10.0	60.0	30.0	1.3677	2.87	83.4
8	0	66.5	33.5	1.3144	2.15	88.1

[a] Relative to water.

± 0.01 °C by circulating water in a surrounding jacket. The drop formation rate and temperature were allowed to stabilize for 45 min. Each surface tension determination was the average of three separate runs, in each of which about 25 drops were collected in a vial with a long narrow neck to minimize loss by evaporation. Under these conditions, the reproducibility in measured surface tension was at least 1%, and more often better.

The outside diameter of the flat capillary tip at which drops formed was 2.74 mm. The surface tension was calculated from the Tate equation

$$mg = 2\pi r\gamma f \quad (1)$$

We chose an average value of *f* from the tables of Harkins and Brown (*3*). To check the apparatus, the surface tensions of pure H_2O, PG, glycerin, and nitrobenzene at 25 °C were measured, and calculated from eq 1. These apparent values, γ_{app}, were compared with literature values (*1, 4*). There was a small discrepancy between experimental and literature values and this was allowed for by "correcting" the apparent values according to the linear relation

$$\gamma_{corr} = 0.964\gamma_{app} + 4.60 \quad (2)$$

This discrepancy probably resulted from (a) a constant (average) value having been taken for *f*, (b) some irreducible vibration, and (c) possible differences in the quality of liquids used in this work as compared with those used in literature studies. Our main purpose was not to determine γ values with great accuracy, but rather to establish the comparative effectiveness of surfactants as surface tension control agents in various solvent media. Equation 2 provided a very convenient way of meeting this requirement, at the same time offering an empirical method of relating precisely measured values with absolute quantities.

Results

Densities, viscosities and surface tensions of the binary solutions NH_4NO_3–H_2O, $NaNO_3$–H_2O, and H_2O–PG are documented in the literature (*1, 4*). We do not report here our measurements on these systems; we used them mainly as a check on our techniques. The measured and literature values, for the most part, agreed within experimental uncertainty.

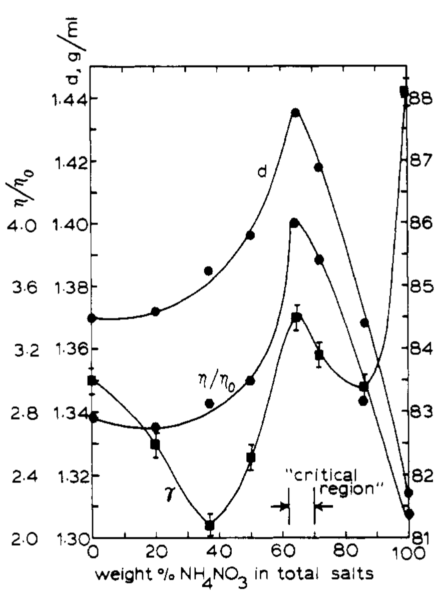

Figure 1. Densities (*d*), relative viscosities (η/η_0), and surface tensions (γ) of solutions near saturation in the system $NaNO_3$–NH_4NO_3–H_2O at 25 °C. The "critical region" represents the interval in composition of salts in solutions for which the equilibrium solid phase is $2NaNO_3 \cdot NH_4NO_3$. Unless indicated otherwise, experimental uncertainty in measured quantities is less than the size of the symbol.

The solubilities of $NaNO_3$ or NH_4NO_3 in various solvents were obtained by an indirect procedure, as follows. The densities of solutions at and near saturation were obtained. A graph of density vs. concentration in the unsaturated solutions was then extrapolated a short distance to the density at saturation, and the corresponding concentration was read off. This concentration was taken as the solubility of the salt in the solvent concerned.

(*a*) ***Binary Systems.*** Table I presents density data of saturated and unsaturated solutions of $NaNO_3$–PG and NH_4NO_3–PG at 25 °C.

(*b*) ***Ternary Systems.*** (*I*) ***$NaNO_3$–NH_4NO_3–H_2O.*** The phase diagram for this system at 25 °C is known (*6*). We chose a number of solutions very close to the curve of saturation, and measured their densities, viscosities, and surface tension. Table II presents these data. Solutions 5 and 6 in this table represent two systems close to that part of the saturation curve for which the solid in equilibrium is the double salt $2NaNO_3 \cdot NH_4NO_3$. The data of Table II are plotted in Figure 1, which shows maxima in all three solution properties in this critical region. The maxima are in fact shown by solution 5. It is to be noted that solution 5 is closest to the saturated solution of highest total salt-to-water ratio (*6*).

(*II*) ***$NaNO_3$–NH_4NO_3–PG.*** Table III presents density and

Table III. Densities and Relative Viscosities[a] of Solutions at or Near Saturation in the System $NaNO_3$–NH_4NO_3–PG at 25 °C

	Comp wt %				
Solution no.	$NaNO_3$	NH_4NO_3	PG	η/η_0	*d*
1	6.24	0	93.76	1.30	1.0724
2	3.13	8.93	87.94	1.21	1.0860
3	1.75	12.86	85.39	1.18	1.0918
4	1.02	14.95	84.03	1.16	1.0953
5	0	17.83	82.17	1.02	1.1040

[a] Relative to PG.

Table IV. Densities, Relative Viscosities,[a] and Surface Tensions of Saturated Solutions in the System $NaNO_3$–H_2O–PG at 25 °C

Composition of mixed solvent, volume %		Solubility[b]			
H_2O	PG	of $NaNO_3$	d	η/η_0	γ
0	100	6.65	1.0724	1.30	36.6
20	80	13.5	1.1106	1.25	39.3
33	67	20.5	1.1443	1.25	40.7
50	50	32.0	1.1908	1.14	43.4
67	33	47.5	1.2533	1.55	47.1
80	20	63.0	1.3094	1.94	51.0
100	0	91.5	1.3742	2.79	83.5

[a] Relative to the (mixed) solvent. [b] In g per 100 g of solvent.

Table V. Densities, Relative Viscosities,[a] and Surface Tensions of Saturated Solutions in the System NH_4NO_3–H_2O–PG at 25 °C

Composition of mixed solvent, volume %		Solubility[b]			
H_2O	PG	of NH_4NO_3	d	η/η_0	γ
0	100	21.7	1.1040	1.02	37.8
20	80	46.0	1.1554	0.780	41.4
33	67	61.0	1.1830	0.731	45.0
50	50	98.0	1.2333	0.661	49.5
67	33	129	1.2691	0.948	51.5
80	20	156	1.2910	1.22	56.6
100	0	205	1.3144	2.14	88.1

[a] Relative to the (mixed) solvent. [b] In g per 100 g of solvent.

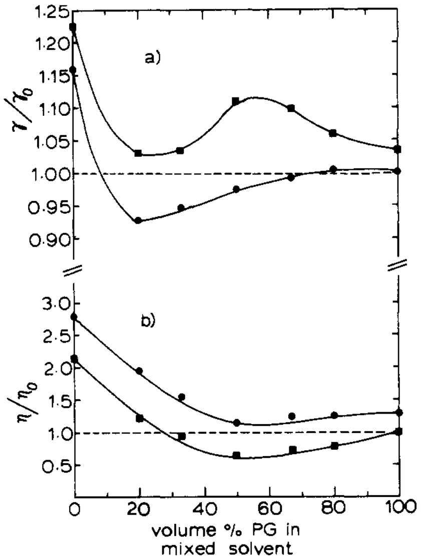

Figure 2. Relative viscosities (η/η_0) and relative surface tensions (γ/γ_0) of saturated solutions of $NaNO_3$ (●) and NH_4NO_3 (■) in mixed solvent H_2O + PG at 25 °C. The reference liquid is the mixed solvent in each case. Experimental uncertainty in measured quantities is less than the size of the symbol in each case.

viscosity data for three ternary solutions (no. 2, 3, 4) near saturation. These ternary solutions were prepared by mixing the two saturated binary solutions (no. 1, 5) in different volume ratios; data for these binaries are also given in the table. No attempt was made to determine the solubility of one salt in the presence of the other in this system.

(iii) $NaNO_3$–H_2O–PG and (iv) NH_4NO_3–H_2O–PG. The data for these systems are presented in Tables IV and V as solution properties at saturation of the salt in the mixed solvent H_2O + PG at various solvent compositions. The viscosity and surface tension data are plotted in Figure 2; for convenience, both properties are expressed relative to that of the solvent in each case. Each pair of curves in the figure shows roughly parallel behavior; however, in (a) the upper curve is the ammonium salt system, whereas in (b) the sodium curve is uppermost. Most (if not all) previous theoretical and experimental work on viscosity (*2*) and surface tension (*5, 8*) of salt solutions has concerned dilute solutions using single solvents. The present data thus cannot be readily interpreted, although one might speculate on the reason for values of γ/γ_0 less than unity for $NaNO_3$ in Figure 2a, given the fact that addition of electrolyte to a solvent raises the surface tension (*5, 8*). The presence of a sufficiently large concentration of organic impurity is ruled out since $\gamma/\gamma_0 > 1$ for the pure water solutions. In the $NaNO_3$ solutions for which $\gamma/\gamma_0 < 1$, the salt may be preferentially solvated by water, and hence may remove a fraction of the water from the bulk (and surface) of the solution. The solvent thus becomes more organic and the surface tension is lowered, even though the solvent is water-rich overall. The ammonium ion is less hydrated than the sodium ion, which may account for the fact that γ/γ_0 for NH_4NO_3 is always greater than unity.

Glossary

γ	surface tension, dyn cm^{-1}
γ_{app}	apparent surface tension, eq 2, dyn cm^{-1}
γ_{corr}	corrected surface tension, eq 2, dyn cm^{-1}
γ/γ_0	relative surface tension
d	density, g mL^{-1}
η/η_0	relative viscosity
f	correction factor (unitless) in eq 1 for determination of surface tension
g	local acceleration of gravity, cm s^{-2}
m	mass in grams of a single drop of liquid in determination of surface tension
r	outside radius, cm, of capillary used in determination of surface tension

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