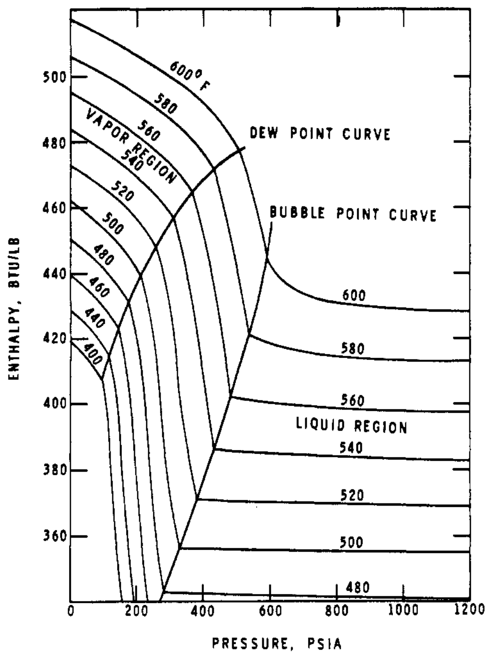

Figure 1. Enthalpy of the mixture 35.2 wt % benzene, 51.5 wt % octane, and 13.3 wt % tetralin

sure and temperature for the mixture with 10 mol % tetralin, with a cricondentherm computed to be 612°F (*3*). The cricondentherm for the case of the $33^1/_3$ mol % tetralin mixture is estimated to be 685°F, and without tetralin, it is determined (*5*) to be 556°F. The two-phase region enlarges as the tetralin content increases. The difference in the gas phase between the measured enthalpy and the ideal gas state enthalpy becomes progressively larger as the tetralin content increases. In the liquid phase, the addition of tetralin decreases the enthalpy. These changes are not linearly dependent on tetralin mole fraction or weight fraction, and illustrate that the mixture of benzene–octane–tetralin does not exhibit simple behavior.

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Separation of Scandium and Calcium by Liquid-Liquid Extraction Using Tri-*n*-butyl Phosphate as Solvent

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The separation of scandium from calcium by solvent extraction at trace-level concentrations has been studied by several investigators. In the isolation of carrier-free calcium from fast-neutron-irradiated scandium from HCl solutions using tri-*n*-butyl phosphate (hereafter TBP) as the solvent, the maximum distribution coefficient for scandium was in 8*N* HCl solutions (*4*). In solutions with a constant, high-chloride-ion concentration (e.g., 11*N* LiCl and HCl), the scandium distribution coefficient was independent of acid concentration. In 7-9*N* HCl solutions, the degree of extraction of scandium was much greater than that of calcium; in fact, the ratio of distribution coefficients was of the order of 200.

When extracting scandium with TBP from $CaCl_2$ and HCl solutions, Romanova et al. (*6*) found that increasing the concentration of $CaCl_2$ increased the amount of scandium extracted. They concluded that scandium can be extracted with high yield both from neutral and acidic solutions. Data for the extraction of scandium and the rare earths distributed between TBP and aqueous solutions containing 3-8*M* HCl have been reported by Peppard et al. (*5*).

Although the distribution coefficients of elements are lower for the TBP–nitrate systems as compared with the TBP–HCl system (*2*), the former system is more selective for certain elements.

Separation and purification of scandium and some actinide and lanthanide elements using the solvent TBP to extract the metal values from nitrate solutions of relatively high acidity look promising. The purpose of this study was to obtain distribution coefficient and separation factor data at concentrations greater than trace level so that these data can be used in the recovery of scandium from a slag which results during the preparation of very pure scandium metal from its oxide.

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Equilibrium data were obtained for the systems $Ca(NO_3)_2$–HNO_3–TBP–H_2O and $Sc(NO_3)_3$–$Ca(NO_3)_2$–HNO_3–TBP–H_2O over a wide range of concentration of the metal nitrates in aqueous solution. Equilibrium acid concentration was used as a parameter for the equilibrium curves. For the system $Sc(NO_3)_3$–$Ca(NO_3)_2$–HNO_3–TBP–H_2O, the distribution coefficients of scandium and calcium decreased with increasing acidity of the aqueous phase. The distribution coefficient of scandium was largely dependent on the total salt concentration in the aqueous phase. The solvent TBP was more highly selective for scandium than for calcium. The separation factor of scandium with respect to calcium was in the range 11–295 depending on the total metal nitrate concentration in the aqueous phase and the acidity of the aqueous phase, but it was not a function of the ratio of scandium to calcium in the aqueous phase.

EXPERIMENTAL

Materials. The scandium used in this study was obtained as the oxide from Alpha Inorganics. The purity of the oxide was 99.9%. Calcium nitrate of reagent grade was obtained from Fisher Scientific Co.

The TBP used was Fisher Scientific Co. purified grade TBP. All TBP used was washed a minimum of four times with demineralized water and stored in contact with water.

The nitric acid used was reagent grade.

Procedure. The scandium oxide was reacted with excess nitric acid, and the excess acid was removed by boiling. The primary stock solution of calcium nitrate was prepared by dissolving the appropriate amount of crystalline material in the form of $Ca(NO_3)_2 \cdot 4H_2O$ in demineralized water. The correct amount of each primary stock solution was measured volumetrically and nitric acid and water were added to give the desired feed concentration and acidity.

A known volume of aqueous feed solution was equilibrated with an equal volume of the organic solvent (undiluted TBP) in a separatory funnel by shaking the two phases vigorously for three minutes, allowing the phases to separate for at least 1 hr and then shaking vigorously for an additional 2 min. The separatory funnel was then allowed to sit undisturbed for at least 10 hr before the phases were separated and the analysis was begun.

All experiments were carried out at constant temperature (25 ± 1°C), and ample time was allowed for equilibrium to be attained; therefore, temperature- and time-dependent effects are not considered in the discussion of the experimental results.

After separation of the aqueous phase, the organic phase was contacted four times with equal volumes of demineralized water to strip the solutes from the solvent. The aqueous strip solution was then analyzed for scandium and calcium content.

The total metal concentration (calcium and scandium) in the initial and final aqueous solutions and in the organic back-extract was determined by EDTA titration using NH_4Cl–NH_4OH buffer and Eriochrome Black T as the indicator at pH 10. An excess of EDTA was added to the aliquot which was then back-titrated with a magnesium chloride solution of known concentration.

The scandium concentration in the initial and final aqueous solutions, and in the organic back-extract, was determined by EDTA titration (*3*) using hexamethylenetetramine as buffer and xylenol orange as indicator at pH 3.5 to 4. The calcium concentration was obtained by difference.

The acidity of the initial and final aqueous solutions was measured by an ion-exchange technique (*1*) using the cation-exchange resin Dowex-50X8. The cation-exchange resin exchanged three hydrogen ions for one scandium ion and two hydrogen ions for one calcium ion; then total hydrogen ion present was titrated with standardized sodium hydroxide using phenolphthalein as indicator.

The EDTA was standardized by titrating with a standard calcium solution prepared by dissolving a known amount of analytical reagent-grade calcium carbonate in dilute (3:1) hydrochloric acid and diluting to a known volume with demineralized water. The titration was performed using Eriochrome Black T as the indicator and NH_4Cl–NH_4OH as buffer at pH 10.

All of the analytical procedures employed are well-accepted volumetric methods. The calcium determination in calcium–scandium mixtures and the acid concentrations are determined by difference and may be less accurate than the direct measurements. The distribution coefficient is the ratio of the concentration of a particular metal in the organic phase and the concentration of that metal in the aqueous phase. The separation factor, $\beta_{Sc/Ca}$, is the ratio of the distribution coefficient of scandium and the distribution coefficient of calcium when both metals are present. Distribution coefficients and separation factors are calculated from the measured concentrations. On the basis of four replications, when the separation factor was relatively low (approximately 20), the standard deviation was 1.066 and the 95% confidence limit for $\beta_{Sc/Ca}$ was ±2.09. For a high value of separation factor (about 120), the standard deviation with three degrees of freedom was 4.68, and the 95% confidence limit on $\beta_{Sc/Ca}$ was ±7.45.

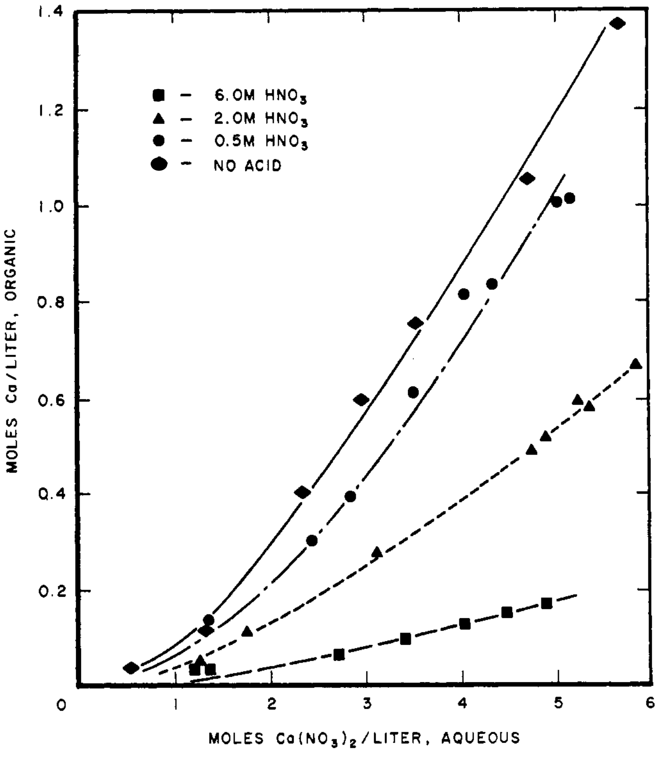

Figure 1. Equilibrium data for the system $Ca(NO_3)_2$–HNO_3–TBP–H_2O

RESULTS AND DISCUSSION

Equilibrium data for the system $Ca(NO_3)_2$–HNO_3–TBP–H_2O are presented in Table I and Figure 1 for aqueous acidities of 0*M*, 0.5*M*, 2*M*, and 6*M* HNO_3.

With no acid in the aqueous phase, the solute concentration in the organic phase increased sharply with increasing aqueous phase concentration. From 2.2*M* to about 5.5*M* calcium nitrate concentration in the aqueous phase, the equilibrium curve was almost linear, indicating a nearly constant distribution coefficient. As the aqueous acidity increased, the solute concentration in the organic phase decreased for a particular aqueous phase solute concentration. In other words, the distribution coefficient decreased with increasing acidity.

The experimental results for the system $Sc(NO_3)_3$–$Ca(NO_3)_2$–HNO_3–TBP–H_2O are given in Table II for aqueous acidities 0*M*, 0.2*M*, 0.8*M*, and 2.45*M* HNO_3.

Table II indicates that the organic phase concentration of scandium depends primarily on the total metal nitrate concentration rather than on the aqueous scandium concentration, as might be expected. Figure 2 shows the scandium distribution coefficient variation with total metal concentration in the aqueous phase using acid concentration as a parameter. The distribution coefficient of scandium increased monotonically with increasing total metal nitrate concentration at constant aqueous acidity, but the slopes of the curves decreased with increasing acid concentration in the aqueous phase (i.e., the scandium distribution coefficient decreased with increasing aqueous acidity). The distribution coefficients of calcium in the system $Ca(NO_3)_2$–HNO_3–TBP–H_2O were generally lower than those obtained in the $Ca(NO_3)_2$–HNO_3–TBP–H_2O system. This was probably due to the greater affinity of the solvent TBP for scandium than for calcium, thereby reducing the amount of calcium extracted.

Table I. Equilibrium Data for System $Ca(NO_3)_2$–HNO_3–H_2O–TBP

Concn of $Ca(NO_3)_2$ in equilib aq phase, mol/l.	Concn of HNO_3 in equilib aq phase, mol/l.	Concn of calcium in equilib org phase, mol/l.	Distribution coeff, $(E_a°)_{Ca}$
0.57	0.000	0.039	0.067
1.35	0.000	0.121	0.089
2.36	0.000	0.405	0.171
2.99	0.000	0.598	0.200
3.58	0.000	0.756	0.211
4.73	0.000	1.05	0.222
5.27	0.000	1.20	0.227
5.30	0.000	1.20	0.225
5.68	0.000	1.36	0.240
1.36	0.470	0.136	0.100
2.43	0.480	0.304	0.124
2.84	0.500	0.394	0.138
3.52	0.501	0.609	0.173
4.08	0.490	0.816	0.200
4.33	0.510	0.839	0.194
5.03	0.501	1.01	0.199
5.14	0.500	1.01	0.197
1.22	2.08	0.054	0.044
1.76	2.06	0.120	0.068
3.12	2.08	0.272	0.087
4.74	2.06	0.487	0.103
4.88	2.04	0.516	0.105
5.23	1.98	0.595	0.114
5.30	2.04	0.571	0.107
5.82	2.00	0.663	0.114
1.22	5.96	0.054	0.043
1.35	5.98	0.040	0.030
2.71	6.00	0.067	0.025
3.40	6.02	0.095	0.028
4.06	6.00	0.135	0.033
4.90	5.96	0.177	0.036

Separation factors, $\beta_{Sc/Ca}$, for the system $Ca(NO_3)_2$–$Sc(NO_3)_3$–HNO_3–TBP–H_2O are tabulated in the last column of Tables II and III and are also represented in Figure 3. Figure 3 shows that with increasing total metal nitrate concentration in the aqueous phase, the separation factors also increased. Inasmuch as the neutral solvent TBP extracts only the un-ionized species in the aqueous phase, it could be predicted that extraction would be better at higher aqueous concentrations because, as the total metal concentration is increased, the proportion of the un-ionized species is also

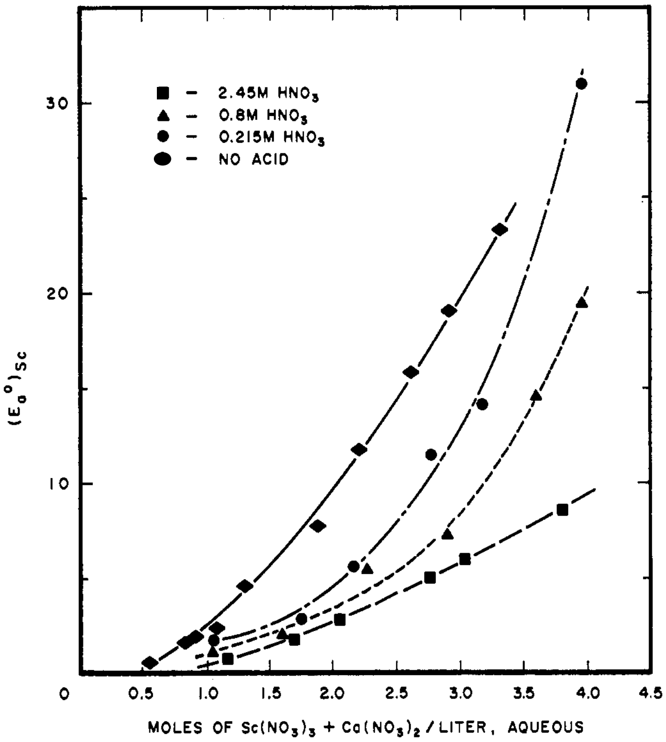

Figure 2. Equilibrium data for the system $Sc(NO_3)_3$–$Ca(NO_3)_2$–HNO_3–TBP–H_2O

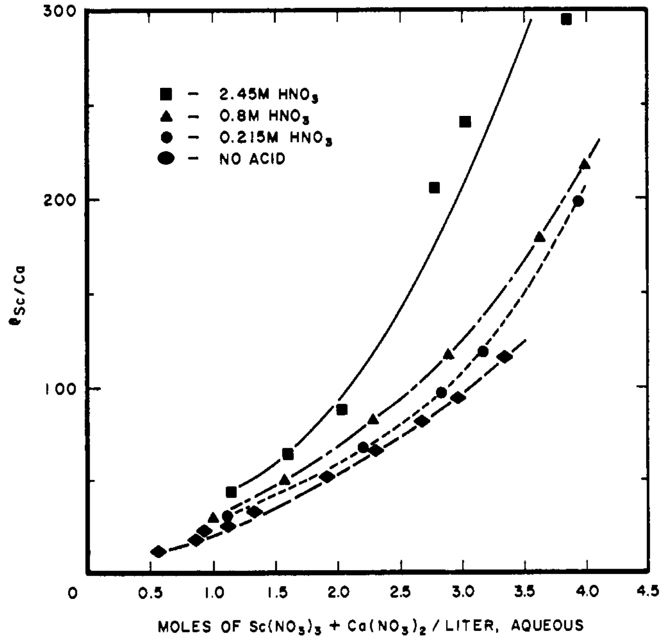

Figure 3. Separation factors for the system $Sc(NO_3)_3$–$Ca(NO_3)_2$–HNO_3–TBP–H_2O

Table II. Equilibrium Data for System $Sc(NO_3)_3$–$Ca(NO_3)_2$–HNO_3–H_2O–TBP

Initial total nitrate concn, mol/l.	Initial ratio, Sc:Ca	Equilib aq concn, mol/l.		Equilib aq acidity, mol/l.	Equilib org concn, mol/l.		$(E_a°)_{Ca}$	$(E_a°)_{Sc}$	$\beta_{Sc/Ca}$
		Ca	Sc		Ca	Sc			
0.664	1:117	0.528	0.0039	0.000	0.0245	0.0021	0.0463	0.54	11.6
0.984	1:103	0.848	0.0032	0.000	0.0693	0.0051	0.0817	1.59	19.5
1.01	1:107	0.861	0.0033	0.000	0.0691	0.0053	0.0802	1.60	19.9
1.05	1:111	0.901	0.0032	0.000	0.0744	0.0054	0.0825	1.70	20.4
1.20	1:98	1.06	0.0040	0.000	0.0984	0.0080	0.0928	2.00	21.6
1.46	1:91	1.33	0.0029	0.000	0.188	0.0133	0.142	4.60	32.4
2.41	1:99	1.87	0.0030	0.000	0.274	0.0230	0.146	7.67	52.5
2.53	1:104	2.26	0.0020	0.000	0.390	0.0230	0.173	11.5	66.8
3.19	1:110	2.66	0.0017	0.000	0.520	0.0270	0.196	15.9	81.0
3.35	1:75	2.94	0.0023	0.000	0.585	0.0432	0.199	18.9	95.0
3.86	1:112	3.36	0.0014	0.000	0.672	0.0327	0.200	23.4	117
1.20	1:100	1.06	0.0040	0.218	0.0636	0.0070	0.0580	1.75	30.1
1.86	1:100	1.72	0.0050	0.220	0.120	0.0140	0.0695	2.80	40.3
2.39	1:120	2.19	0.0030	0.219	0.184	0.0170	0.0840	5.66	67.5
2.93	1:132	2.79	0.0020	0.214	0.334	0.0230	0.120	11.5	96.3
3.59	1:132	3.19	0.0018	0.220	0.382	0.0260	0.120	14.2	119
4.39	1:136	3.86	0.0010	0.207	0.593	0.0310	0.154	31.0	201
1.06	1:90	1.02	0.0058	0.800	0.0400	0.0063	0.0394	1.08	27.4
1.72	1:90	1.59	0.0063	0.802	0.0665	0.0130	0.0416	2.08	50.0
2.38	1:102	2.26	0.0040	0.808	0.139	0.0202	0.0617	5.05	81.8
3.12	1:103	2.92	0.0039	0.794	0.186	0.0288	0.0635	7.38	116
3.86	1:110	3.65	0.0023	0.800	0.299	0.0335	0.0818	14.6	178
4.26	1:105	3.99	0.0020	0.798	0.360	0.0390	0.0902	19.5	216
1.20	1:120	1.13	0.0048	2.46	0.027	0.0048	0.0239	1.00	42.0
1.73	1:115	1.69	0.0056	2.48	0.0453	0.0101	0.0274	1.80	657
2.13	1:106	2.04	0.0055	2.46	0.0664	0.0160	0.0325	2.91	89.6
2.93	1:133	2.79	0.0039	2.43	0.0691	0.0199	0.0247	5.10	207
3.19	1:106	3.05	0.0038	2.42	0.133	0.0288	0.0228	6.00	240
4.26	1:142	3.85	0.0036	2.41	0.107	0.0296	0.0278	8.22	296

Table III. Equilibrium Data for System $Sc(NO_3)_3$–$Ca(NO_3)_2$–TBP–H_2O at Constant Initial Total Nitrate Concentration

Initial total nitrate concn, mol/l.	Initial ratio, Sc:Ca	Equilib aq concn, mol/l.		Equilib org concn, mol/l.		$(E_a°)_{Ca}$	$(E_a°)_{Sc}$	$\beta_{Sc/Ca}$
		Ca	Sc	Ca	Sc			
2.57	1:55	2.29	0.0038	0.336	0.0421	0.146	11.1	75.6
2.57	1:38	2.26	0.0054	0.314	0.0577	0.139	10.7	77.1
2.57	1:37	2.15	0.007	0.311	0.074	0.144	10.6	73.4
2.57	1:21	2.30	0.011	0.313	0.112	0.136	10.2	74.9
2.57	1:15	2.15	0.016	0.264	0.148	0.123	9.25	75.2

increased. The rise in the distribution coefficients of both calcium and scandium with increasing total metal nitrate concentration may be attributed to increased concentrations of un-ionized scandium and calcium species in the aqueous phase. The trivalent scandium may be preferentially extracted at high ionic strength because of a greater tendency to form a neutral species in aqueous solution.

The separation factors for the system $Sc(NO_3)_3$–$Ca(NO_3)_2$–HNO_3–TBP–H_2O increased with increasing aqueous phase acidities while the distribution coefficients of both calcium and scandium were decreasing. The distribution coefficient of calcium decreased to a greater extent than did the scandium distribution coefficient. As the acid concentration in the aqueous phase was increased, more acid was extracted into the organic phase creating competition between the acid and the un-ionized metal species for the solvent. Thus, the distribution coefficients of the metal nitrates were lowered. In other words, the decrease in the distribution coefficient with increasing acidity is due to the loading of the organic phase with HNO_3, so that there is less TBP available for extraction of metal-containing species.

The decrease in the amount of solute extracted at higher acidities (lower distribution coefficients) is evident from the data presented in Tables I and II. For example, when the initial total metal nitrate concentration was 1.20*M* (initial scandium concentration, approximately 0.01*M*), the fraction of available scandium transferred to the organic phase decreased from 67% with no acid in the aqueous phase to 50% when the aqueous phase acidity was increased to 2.45*M*, although the separation factor was higher in the latter experiment.

The results tabulated in Table III show that varying the ratio of the scandium and calcium nitrates in the aqueous phase, while maintaining constant the total metal nitrate concentration in the aqueous phase, had no effect on the separation factor. Since the mechanism of extraction for TBP is by direct solvation and not by ion exchange, the separation factor is largely dependent upon the total concentration of solutes in the aqueous phase, and not on the concentration of the individual solutes. The results obtained are consistent with those reported by Smutz and Gray (*7*) for the system $NdCl_3$–$PrCl_3$–HCl–TBP–H_2O, where the separation factor was not dependent upon the ratio of the two rare earths.

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Flammability Properties of Hydrocarbon Solutions in Air

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Work on the interrelations of the flammability properties of *n*-alkanes in air has been extended to both vapor and liquid fuel mixtures. By application of Raoult's and Dalton's laws governing vapor pressure and composition above a solution of two or more liquid hydrocarbons to Le Chatelier's rule governing the flammability limits of vapor mixtures, equations have been derived which make it possible to predict overall flammability properties of mixtures from the properties and proportions of the individual components. The properties which were studied include: lower and upper flammability limits, heat of combustion, stoichiometric concentration, flash point, and flammability index ("explosiveness"). Experimentally determined flash points of multicomponent solutions were in good agreement with the calculated values, confirming the point that hydrocarbon solutions follow the above laws, and also confirming the concept of flash point as that temperature at which the vapor concentration above a liquid is equal to that at its lower flammability limit. The derived equations demonstrate why vapor pressure of individual constituents plays a more important role than concentration on the overall flammability properties of liquid solutions, and that a very small amount of a highly volatile contaminant in a relatively nonflammable fuel may make it flammable.

As a result of improper preparation, contamination, or other reasons, less volatile liquid combustibles may sometimes contain small quantities of highly volatile flammable components which can significantly influence the overall flammability properties of the mixture. It would be useful to be able to predict these and relate the effects quantitatively. Some physical properties of liquid solutions, such as density, are generally proportional to the properties and concentrations of the individual components. Combustion, on the other hand, occurs in the vapor phase; hence flammability is a function of vapor concentration above the liquid. Therefore, combustion depends not only on the flammability properties and concentrations (both vapor and liquid), but also to a marked degree on the vapor pressures of the individual components of the solution.

From the standpoint of fire hazard in the storage and handling of flammable liquids and fuels, more knowledge is needed concerning the flammability properties of multicomponent liquid mixtures. The flammability properties to be discussed are lower and upper flammability limits, heat of combustion, stoichiometric concentration (for complete oxidation), flash point, and flammability index.

PRINCIPLES INVOLVED

Le Chatelier's rule governing the flammability limits of vapor mixtures (*16*) and the useful rearrangement of this formula by Coward et al. (*9*) have been known for a long time. These equations, summarized by Coward and Jones (*10*) and more recently by Zabetakis (*22*), have been found to be applicable to hydrocarbon vapor mixtures (*10, 19, 22*) for both lower and upper flammability limits (*9, 13, 18*).

For liquid solutions, it is necessary to determine the vapor composition above the liquid before application of Le Chatelier's rule. Since hydrocarbon solutions do not deviate appreciably from Raoult's Law (*17, 22*), a combination of Raoult's and Dalton's laws govern vapor pressure and composition above a solution of two or more liquids. This treatment has been applied to lower flammability limits of liquid solutions containing methyl ethyl ketone and tetrahydrofuran by Zabetakis et al. (*23*). Zabetakis (*22*) also reported its application to flammability limits of two-component liquid hydrocarbon mixtures. Empirical formulas making use of certain of these concepts for calculating flash points of complex mixtures and blends were reported by Thiele (*20*), Butler et al. (*8*), and Mullins (*18*).

As a continuation of previous work at this laboratory on the interrelations of the flammability properties of the *n*-alkanes in air (*1*), it was decided to extend some of the derived relationships to both vapor and liquid hydrocarbon mixtures in order to predict overall flammability properties from the properties and proportions of the individual components.

LIMITATIONS

The present discussion will be limited to liquid and vapor hydrocarbon fuels, excluding droplets and mists, in air at atmospheric pressure. It will be assumed that the vapor is in equilibrium with the liquid at a given temperature, and that

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