Table III. Experimental Data for Ternary Nitroethane–Hydrocarbon Systems.

Nitroethane–n-Octane–1-Octene Wt. Fractions at 0.0° ± 0.05° C

Nitroethane	n-Octane	Nitroethane	n-Octane
0.058	0.942^a	0.291	0.107
0.077	0.718	0.340	0.078
0.079/0.886	0.668/0.083	0.506	0.045
0.099/0.852	0.515/0.070	0.529	0.041
0.126/0.812	0.371/0.065	0.747	0.048
0.152	0.269	0.806	0.057
0.174	0.233	0.832	0.066
0.240	0.155	0.910^a	0.090

Nitroethane–n-Octane–2,2,4-Trimethylpentane Wt. Fractions at 25.0° ± 0.05° C.

Nitroethane	n-Octane
0.137/0.826	0.786/0.157
0.149/0.797	0.519/0.120
0.168/0.764	0.334/0.085

Nitroethane–n-Octane–2,2,4-Trimethylpentane Wt. Fractions at 35.0° ± 0.05° C.

Nitroethane	n-Octane	Nitroethane	n-Octane
0.718	0.237	0.301/0.637	0.347/0.184
0.591	0.169	0.270	0.480
0.568	0.167	0.263/0.699	0.528/0.217
0.405	0.221	0.262	0.503
0.319/0.621	0.319/0.172	0.260/0.721	0.619/0.233

entries refer to cloud point determinations. The chromatographic method of analysis used in the determination of the tie-lines was subject to some error. The tie-line data, however, are in good agreement with the binodal curve determined from the cloud-point measurements.

DISCUSSION

Mutual solubility data obtained from a smoothed plot of the experimental data were used to evaluate the two parameters of the van Laar activity coefficient equations for all systems; of the Margules equations for the n-hexane, 2-methylpentane, and n-octane systems; and of the Scatchard-Hamer equations for the n-hexane and 2-methylpentane systems (*6*). The ratios of the van Laar parameters A and B were in all instances less than 1.5 indicating that the van Laar and Margules equations should be equally applicable to these systems (*10*). The difference between the activity coefficients calculated by the van Laar and Margules equations was negligible for the three systems for which this comparison was made. However, in the dilute homogeneous region, the activity coefficients calculated by the Scatchard-Hamer equations differed considerably from those calculated using the other equations.

Plots of the van Laar parameters, A and B, for each binary system *vs.* the reciprocal of the absolute temperature gave a linear relation up to within a few degrees of the critical solution temperature. Extrapolation of this linear relation may be a useful method for obtaining values of the parameters from which vapor-liquid equilibrium data can be estimated at the temperatures above the critical solution temperature. Vapor-liquid equilibrium measurements are presently being carried for several of these binary and ternary systems to obtain activity coefficient data in the homogeneous region above and below the critical solution temperature. The data will be used to test the applicability of the two-parameter models and the usefulness of the linear extrapolation.

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Solubilities of Anhydrous Ionic Substances in Absolute Methanol

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THE PURPOSE of the experimentation was to determine the effect of ionic size on the solubility of an ionic compound in methanol. Another object of the investigation was to correlate the solubilities in methanol with those in water, as given in the various handbooks of chemistry.

Data in the literature show large discrepancies for solubilities of inorganic substances in methanol (*1–6*). These discrepancies may be attributed to a small amount of water in methanol and to impurities in the solutes.

EXPERIMENTAL

Chemicals. Anhydrous salts of the alkali and alkaline earth metals in combination with the halides, the nitrate,

Solubility values of the common alkali and alkaline earth fluorides, chlorides, bromides, iodides, nitrates, carbonates, and sulfates (where ACS reagents were abailable) have been determined. The solubilities in methanol of the ionic compounds, which were investigated, were comparable with solubilities in water except in the cases of the alkali sulfates and some nitrates. Gradations of solubility with ionic size were the same in methanol as in water except for the alkaline earth fluorides and sulfates.

Table I. Solubilites in Methanol

Grams/100 grams solvent

	Fluoride (1.36)	Chloride (1.81)	Bromide (1.95)	Iodide (2.16)	Nitrate	Carbonate	Sulfate
Lithium (0.60)	0.0176	20.98	34.29	...	42.95	0.0555	0.1261
Sodium (0.95)	0.0231	1.401	16.09	62.51	2.936	0.3109	0.0113
Potassium (1.33)	2.286	0.5335	2.080	17.07	0.3795	6.165	0.0005
Calcium (0.99)	0.0145	23.26	55.83	67.37	127.1	0.0012	0.0046
Strontium (1.13)	0.0142	18.05	...	...	1.061	0.0014	0.0074
Barium (1.35)	0.0044	1.379	...	...	0.0480	0.0064	0.0063

(Ionic radii, A, are indicated in parentheses.)

the carbonate, and the sulfate, were selected as suitable solutes for the study. Only those salts which meet the requirements of the ACS Committee on Analytical Reagents were deemed of sufficient purity to produce reliable results. Such compounds were over 99% pure. The methanol was also ACS Reagent Grade, and analyzed to be 99.8% pure. Omissions in the table of experimental values are due to the unavailability of the compounds in sufficient purity.

Methods. Saturated solutions of the various solutes in methanol were obtained at 25° C. in a constant-temperature, water-bath shaker. Sufficient samples, at various intervals of shaking, were withdrawn to ensure that equilibrium had been reached. After equilibrium had been attained, samples were withdrawn and weighed. Rapidity in sampling and weighing was of critical importance in obtaining satisfactory results. The weighing was accomplished on a single-pan, direct-reading type of balance. The weighed samples were evaporated and dried to constant weight. Solubility results were calculated on the basis of grams of solute per 100 grams of solvent.

DISCUSSION OF RESULTS

Alkali Metal Ions. Salts of strong acids are soluble in methanol except the sulfates. Salts of weak acids are relatively insoluble except KF and K_2CO_3. Solubilities decrease with increase in cation size except in the cases of the fluorides and carbonates.

Solubilities increase with increase of anion size except in the case of KF.

Alkaline Earth Ions. Solubilities decrease with increase in anion size for fluorides, chlorides, and nitrates; however, solubilities increase with cation size for carbonates and sulfates.

Comparison with Water Solubilities. Solubilities in methanol are comparable, although smaller, to those in water except in the case of the alkali sulfates, and some of the nitrates.

Solubilities in methanol differ from those in water inasmuch as the alkaline earth fluorides decrease with cation size in methanol whereas they increase with cation size in water. The solubilities of the alkaline earth sulfates increase with cation size in methanol, but decrease with cation size in water.

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