J. Chem. Eng. Data **1988,** *33,* 465-468

Micellization and Conductometric Investigation on Some Lanthanide Metal Oleates

Krishna N. Mehrotra and Sanjay K. Upadhyaya*

Department of Chemistry, Agra University, Agra 282 004, India

The critical micelle concentration, degree of dissociation, dissociation constant, and thermodynamic parameters for dissociation and micellization processes for lanthanide (La, Ce, and Nd) oleates in a mixture of 60% benzene and 40% methanol were evaluated from the conductivity measurements. The results showed that these soaps behave as weak electrolytes in dilute solutions and the values of the cmc increase with the increasing temperature.

Introduction

The study of metallic soaps is becoming increasingly important in technological as well as in academic fields. It has been a subject of intense investigations in the recent past on account of its role in such diversified fields as detergents, softeners, stabilizers, plasticizers, lubricants, catalysts, cosmetics, medicines, emulsifiers, and water-proofing agents. However, technological applications of these soaps are mostly based on empirical knowhow and the selection of a soap is dependent largely on economic factors.

A survey of literature reveals that the physicochemical studies of alkali-, alkaline-earth-, and transition-metal soaps have been extensive whereas only a few references (*1-16*) are available on rare-earth-metal soaps, although these soaps are being widely used in many industries. The present work deals with the studies on the conductance and micellar behavior of some lanthanide metal (La, Ce, and Nd) soaps in a mixture of 60% benzene and 40% methanol at different temperatures (30-60 °C).

Experimental Section

The lanthanide soaps were prepared by the direct metathesis of corresponding potassium soap with the required amount of lanthanide metal chlorides/nitrates in water-alcohol medium (1:1). The precipitated soaps were washed with water and acetone to remove the excess of metal ions and unreacted oleic acid. Both the preparation and purification processes were carried out under nitrogen atmosphere to protect against possible oxidation of these soaps. The purity of the soaps was checked by the elemental analysis and the results were found in agreement with the theoretically calculated values (Table I). The reproducibility of the results was checked by preparing two samples of the soap under similar conditions. The purified soaps have the following melting points: lanthanum oleate, 138.9 °C; cerium oleate, 140.1 °C; neodymium oleate, 144 °C. The solutions of soaps were prepared by dissolving a known amount of soap in a mixture of 60% benzene and 40% methanol and were kept for 2 h in a thermostat at the desired constant temperature.

The conductance of the solutions was measured with a Toshniwal digital conductivity meter, Model CL 01 10A, and a dipping type conductivity cell (cell constant 0.90) with platinized electrodes at different temperatures.

Table I. Percentages of Elements in Lanthanide Metal Oleates

	carbon		hydrogen		metal	
	found	calcd	found	calcd	found	calcd
lanthanum oleate	65.96	65.99	10.06	10.08	14.14	14.15
cerium oleate	65.89	65.91	10.05	10.07	14.22	14.25
neodymium oleate	65.60	65.64	10.01	10.03	14.60	14.61

Table II. Cmc Values of Lanthanide Metal Soaps in 60% Benzene and 40% Methanol

	cmc × 10^3, mol L^{-1}			
	30 °C	40 °C	50 °C	60 °C
lanthanum oleate	4.4	5.5	7.2	8.5
cerium oleate	4.1	4.9	5.6	6.6
neodymium oleate	4.0	4.6	5.6	6.5

Results and Discussion

The specific conductance, *k*, of the solutions of lanthanide soaps in 60% benzene and 40% methanol (v/v) increases with increase in soap concentration and temperature. The plots of specific conductance vs soap concentration (Figure 1) are characterized by an intersection of two straight lines at a concentration which corresponds to the cmc. The results show that the increase in temperature and decrease of the size of metal ion result in the increase of the cmc (Table II).

The molar conductance, μ, of the dilute solutions of soaps decreases with increasing soap concentration. However, the cmc values cannot be obtained from the plots of molar conductance vs square root of soap concentration (Figure 2) because the plots are concave upwards with increasing slopes, indicating that these soaps behave as weak electrolytes in dilute solutions and Debye-Hückel-Onsager's equation is not applicable to these soap solutions. Since the lanthanide oleates behave as weak electrolytes in dilute solutions, an expression for the dissociation may be developed in Ostwald's manner. The dissociation of lanthanide oleates can be represented as follows

$$\underset{C(1-\alpha)}{M(RCOO)_3} \rightleftharpoons \underset{C\alpha}{M(RCOO)_2{}^+} + \underset{C\alpha}{RCOO^-} \tag{1}$$

$$\underset{C(1-\alpha)}{M(RCOO)_3} \rightleftharpoons \underset{C\alpha}{M(RCOO)^{2+}} + \underset{2(C\alpha)}{2RCOO^-} \tag{2}$$

$$\underset{C(1-\alpha)}{M(RCOO)_3} \rightleftharpoons \underset{C\alpha}{M^{3+}} + \underset{3(C\alpha)}{3RCOO^-} \tag{3}$$

where C is the concentration of soap (g mol L^{-1}), α is the degree of dissociation, and M is lanthanum, cerium, or neodymium. The dissociation constant K_1, K_2, and K_3 for the above dissociations can be expressed as

$$K_1 = \frac{[M(RCOO)_2{}^+][RCOO^-]}{[M(RCOO)_3]} = \frac{C\alpha C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \tag{4}$$

$$K_2 = \frac{[M(RCOO)^{2+}][RCOO^-]^2}{[M(RCOO)_3]} = \frac{C\alpha(2C\alpha)^2}{C(1-\alpha)} = \frac{4C^2\alpha^3}{1-\alpha} \tag{5}$$

$$K_3 = \frac{[M^{3+}][RCOO^-]^3}{[M(RCOO)_3]} = \frac{C\alpha(3C\alpha)^3}{C(1-\alpha)} = \frac{27C^3\alpha^4}{1-\alpha} \tag{6}$$

Since the ionic concentrations in dilute solutions are low and the interionic effects are almost negligible, the soap solutions

0021-9568/88/1733-0465$01.50/0

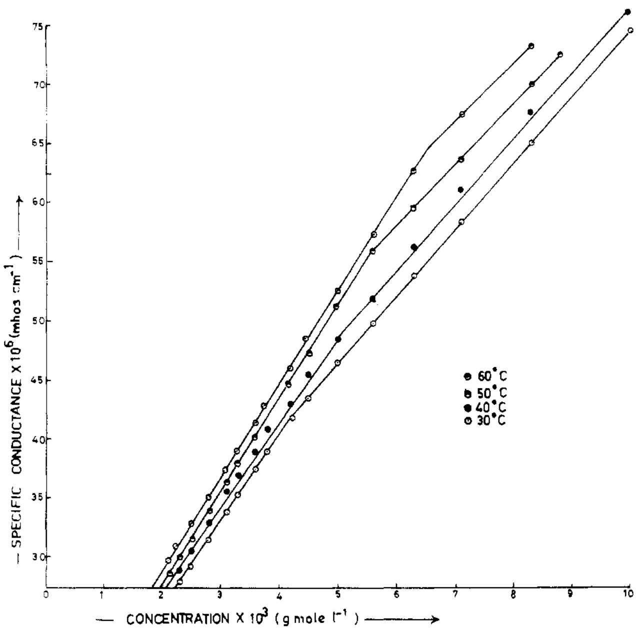

Figure 1. Specific conductance vs concentration plots for cerium in a benzene-methanol mixture.

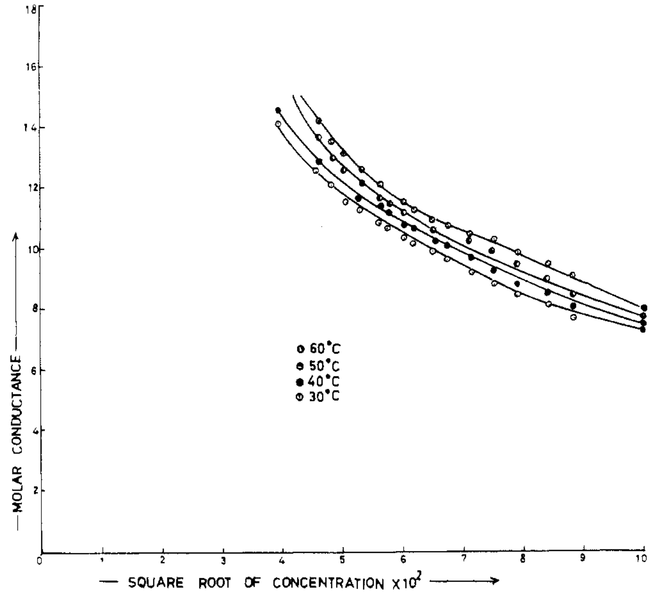

Figure 2. Molar conductance vs square root of concentration plots for cerium oleate.

Table III. Values of Limiting Molar Conductance, μ_0, of Lanthanide Metal Soaps

	30 °C	40 °C	50 °C	60 °C
lanthanum oleate	8.01	8.33	9.19	10.82
cerium oleate	15.14	16.10	16.33	19.13
neodymium oleate	15.80	16.46	17.62	20.00

Table IV. Values of Dissociation Constant of Lanthanide Metal Soaps

	10^3K_1			
	30 °C	40 °C	50 °C	60 °C
lanthanum oleate	1.85	1.37	0.82	0.54
cerium oleate	2.23	1.78	1.39	1.07
neodymium oleate	0.80	0.55	0.42	0.29
	10^5K_2			
	30 °C	40 °C	50 °C	60 °C
lanthanum oleate	6.19	3.37	1.97	1.26
cerium oleate	4.92	3.80	2.49	2.46
neodymium oleate	2.76	1.99	1.41	1.13
	10^7K_3			
	30 °C	40 °C	50 °C	60 °C
lanthanum oleate	13.70	11.70	8.35	4.69
cerium oleate	8.57	6.89	6.07	3.55
neodymium oleate	5.59	5.44	4.15	2.70

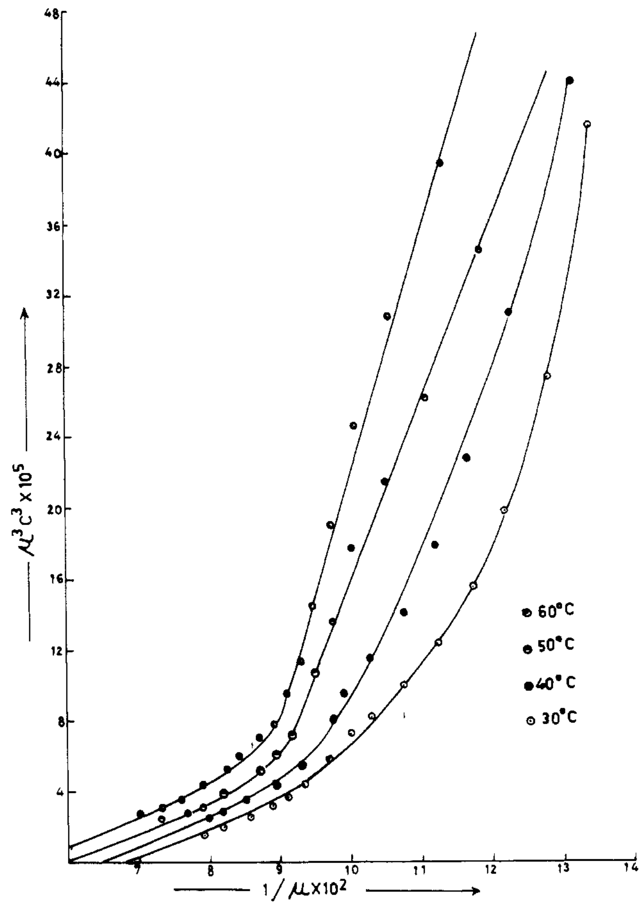

Figure 3. μ^3C^3 vs $1/\mu$ plots for cerium oleate.

will not deviate appreciably from ideal behavior and so the activities of ions can be taken as almost equal to the concentrations. The degree of dissociation may be replaced by the conductance ratio, μ/μ_0, where μ is the molar conductance at finite concentration and μ_0 is the limiting molar conductance at infinite dilution. On substituting the value of α and rearranging, eq 4, 5, and 6 can be written as

$$\mu C = \frac{K_1\mu_0^2}{\mu} - K_1\mu_0 \tag{7}$$

$$\mu^2C^2 = \frac{K_2\mu_0^3}{4\mu} - \frac{K_2\mu_0^2}{4} \tag{8}$$

$$\mu^3C^3 = \frac{K_3\mu_0^4}{27\mu} - \frac{K_3\mu_0^3}{27} \tag{9}$$

The values of dissociation constants, K_1, K_2, and K_3, and limiting molar conductance, μ_0, have been obtained from the slopes and intercepts of the linear portion of the plots of μC vs $1/\mu$, μ^2C^2 vs $1/\mu$, and μ^3C^3 vs $1/\mu$ for dilute soap solutions (Figure 3) and are recorded in Tables III and IV. The values of K_1, K_2, and K_3 were found in the order $K_1 > K_2 > K_3$.

The values of the degree of dissociation at different soap concentrations have been calculated by assuming them as equal to the conductance ratio, μ/μ_0. The results show that the lanthanide soaps behave as weak electrolyte in these solutions.

Table V. Thermodynamic Parameters of Lanthanide Soaps

	ΔH_D,[a] kcal	ΔH_A,[b] kcal
lanthanum oleate	-9.52	-9.62
cerium oleate	-6.79	-6.55
neodymium oleate	-4.58	-6.23

[a] Heat of dissociation. [b] Heat of association.

The values of the degree of dissociation decrease rapidly in dilute solutions with increasing soap concentration whereas the values decrease slowly above the cmc. The decrease in the values of the dissociation constant, K_3, with increasing temperature indicates the exothermic nature of the dissociation of lanthanide soaps in benzene–methanol mixture.

The heats of dissociation, ΔH_D, for lanthanide soap solutions have been calculated by using the expression

$$\frac{\partial(\log K)}{\partial T} = \frac{\Delta H_D}{RT^2}$$

or

$$\log K = -\frac{\Delta H_D}{RT} + C \qquad (10)$$

The values of heat of dissociation, ΔH_D, have been obtained from the slope of the linear plots of log K_3 vs $1/T$ (Figure 4) and are recorded in Table V. The negative values of the heat of dissociation, ΔH_D, indicate that the dissociation process is exothermic in nature.

The values of the change in free energy, ΔG_D, and entropy, ΔS_D, per mole for the dissociation process have been calculated by using the relationships

$$\Delta G_D = -RT \ln K_D \qquad (11)$$

$$\Delta S_D = (\Delta H_D - \Delta G_D)/T \qquad (12)$$

The calculated values of ΔG_D and ΔS_D are recorded in Table VI.

For the aggregation process, when counterions are bound to a micelle, the standard free energy of micellization (per mole of monomer), ΔG_A, for the phase separation model (*17*, *18*) is given by the relationship

$$\Delta G_A = 2RT \ln X_{cmc} \qquad (13)$$

where X_{cmc} is the cmc expressed in terms of mole fraction and is given by the relationship

$$X_{cmc} = n_s/(n_s + n_o)$$

where n_s and n_o are the number of moles of surfactant and solvent, respectively. Since the number of moles of free surfactants, n_s, is small as compared to the number of moles of solvent, n_o, it follows that

$$X_{cmc} = n_s/n_o$$

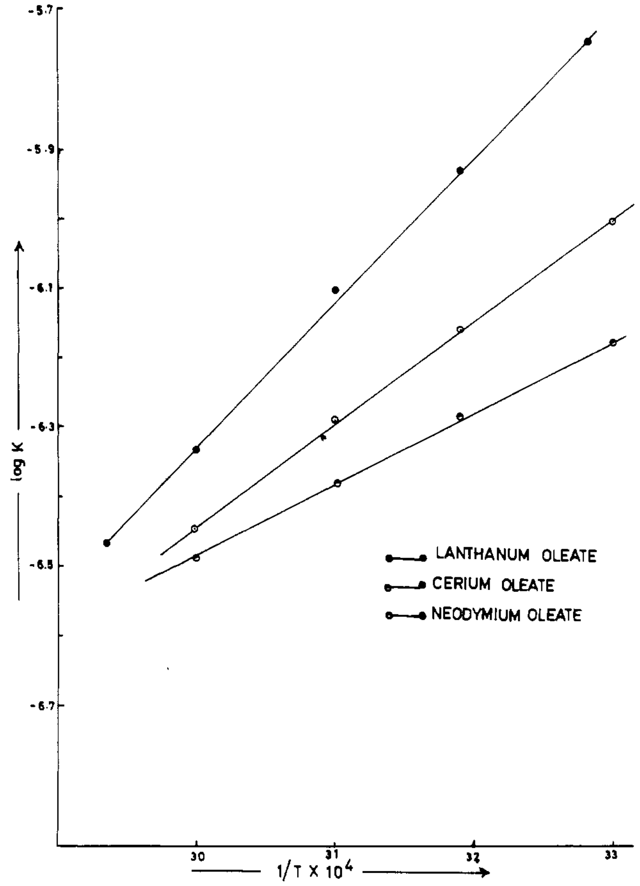

Figure 4. log K vs $1/T$ plots for lanthanide metal oleates.

The standard enthalpy change of micellization per mole of monomer for the phase separation model (*17*, *18*), ΔH_A, is given by the relationship

$$\frac{\partial(\ln X_{cmc})}{T} = -\frac{\Delta H_A}{2RT^2}$$

$$\ln X_{cmc} = \frac{\Delta H_A}{2\,RT} + C \qquad (14)$$

The values of ΔH_A of lanthanide soaps have been obtained from the slope of the linear plots of ln X_{cmc} vs $1/T$ (Figure 5) and are recorded in Table V.

The negative values of ΔG and positive values of ΔS for the micellization process (Table VII) and positive values of ΔG and negative values of ΔS for the dissociation process (Table VI) indicate that micellization is favored over the dissociation process.

It is, therefore, concluded that the thermodynamics of dissociation and association can satisfactorily be explained in light

Table VI. Thermodynamic Parameters for the Dissociation Process

	ΔG_D, kcal				$10^2\Delta S_D$, kcal			
	30 °C	40 °C	50 °C	60 °C	30 °C	40 °C	50 °C	60 °C
lanthanum oleate	2.71	2.84	3.00	3.22	-4.04	-3.95	-3.88	-3.83
cerium oleate	2.81	2.95	3.07	3.28	-3.17	-3.11	-3.05	-3.02
neodymium oleate	2.86	3.00	3.15	3.34	-2.46	-2.42	-2.39	-2.38

Table VII. Thermodynamic Parameters for the Association Process

	ΔG_A, kcal				$10^3\Delta S_A$, kcal			
	30 °C	40 °C	50 °C	60 °C	30 °C	40 °C	50 °C	60 °C
lanthanum oleate	-9.91	-9.96	-9.93	-10.02	0.96	1.09	0.96	1.20
cerium oleate	-10.00	-10.11	-10.26	-10.36	11.39	11.37	11.49	11.44
neodymium oleate	-10.02	-10.18	-10.26	-10.38	12.51	12.62	12.48	12.46

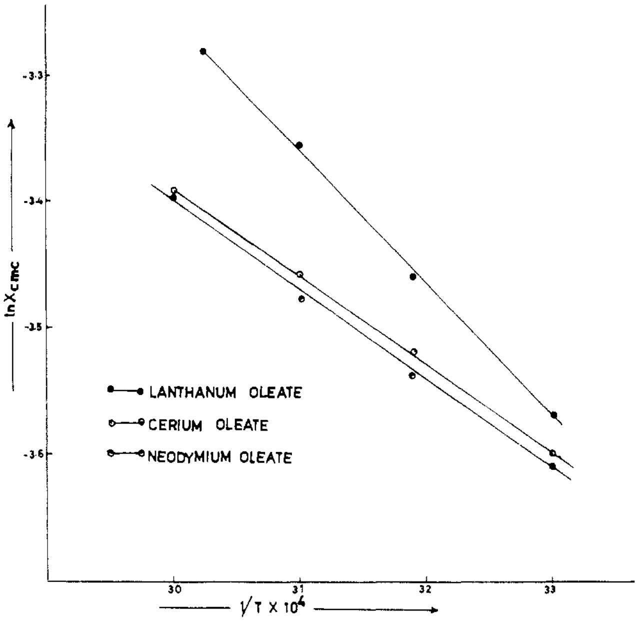

Figure 5. ln X_{cmc} vs $1/T$ plots for lanthanide metal oleates.

of the phase separation model and conductivity measurements. The results showed that the micellization process is predominant over the dissociation process and lanthanide soaps behaved as a weak electrolyte in benzene–methanol mixture.

Registry No. Lanthanum oleate, 94232-46-9; cerium oleate, 94232-60-7; neodymium oleate, 90568-80-2; benzene, 71-43-2; methanol, 67-56-1.

Literature Cited

(1) Mehrotra, R. C. *Wiss. Z. Friedrich-Schiller Univ. Jena Math. Naturwiss. Reihe*. **1965**, *14*, 171.
(2) Skellon, J. H.; Andrews, K. E. *J. Appl. Chem. London*, **1955**, *5*, 245.
(3) Ryan, L. W.; Plechnar, W. W. *Ind. Eng. Chem.* **1934**, *26*, 909.
(4) Chatfield, H. W. *Paint Manuf*. **1936**, *6*, 112.
(5) Skrylev, L. D.; Sazonna, V. F.; Kornelli, M. E.; Shumitina, N. A. *Khim. Khim. Tekhnol*. **1978**, *21*, 491.
(6) Skellon, J. H.; Spence, J. W. *J. Appl. Chem. London*, **1953**, *3*, 10.
(7) Titanium Pigment Co. Inc. Brit. **1933**, *17*, 395–406.
(8) Misra, S. N.; Misra, T. N.; Mehrotra, R. C. *J. Inorg. Nucl. Chem.* **1963**, *25*, 195–201.
(9) Skellon, J. H.; Spence, J. W. *J. Soc. Chem. Ind. London* **1948**, *67*, 365.
(10) Morwedel, G.; *Farbe + Lack* **1954**, *60*, 530, **1956**, *62*, 92.
(11) Main, F.; Mills, D.; White, D. W. U.S. Patent 3 320 172, 1967.
(12) Bhandari, A. M.; Dubey, S.; Kapoor, R. N. *J. Am. Oil Chemist's Soc.* **1970**, *4*, 47.
(13) Solanki, A. K.; Bhandari, A. M. *Tenside Detergents*, **1961**, *18*, 34.
(14) Varma, R. P.; Jindal, R. *Tenside Detergents*, **1983**, *20*, 193.
(15) Mehrotra, K. N.; Gahlaut, A. S.; Sharma, Merra. *J. Am. Oil Chemists Soc*. **1986**, *63*, 1571.
(16) Mehrotra, K. N.; Gahlaut, A. S.; Sharma, Meera, *J. Colloid Interface Sci*. **1987**, *1*(*120*), 110.
(17) Barry, B. W.; Russel, G. F. J. *J. Colloid Interface Sci*. **1972**, *40*, 174.
(18) Robins, D. C.; Thomas, I. L. *J. Colloid Interface Sci*. **1968**, *26*, 407.

Received for review November, 17, 1987. Accepted May 31, 1988. Grateful thanks are extended to UGC, New Delhi, for financial assistance to S.K.U.

Liquid–Liquid Equilibrium Data for the Ternary Systems Water–Ethyl Alcohol–Organic Acid (Hexanoic, Heptanoic, Octanoic, and Nonanoic Acid) and Water–Ethyl Alcohol–Phthalic Acid Dialkyl Ester (Diethyl, Dibutyl, and Dioctyl Ester)

Isidoro G. García,* Arturo Ch. Pérez, and Francisca C. Calero

Departamento de Ingeniería Química, Facultad de Ciencias, C/San Alberto Magno s/n, 14004-Córdoba, Spain

The liquid–liquid equilibrium data for the ternary systems water–ethyl alcohol–organic acid (hexanoic, heptanoic, octanoic, and nonanoic acid) and water–ethyl alcohol–phthalic acid dialkyl ester (diethyl, dibutyl, and dioctyl ester) have been determined at 298 K. The data were compared with those obtained from the UNIFAC method. Finally, densities of the conjugated phases have been determined.

Introduction

The use of ethanol obtained from fermented waste rich in carbohydrates is already well-known (*1*).

Liquid–liquid extraction is a technique known to separate the ethanol from water mixtures; it is an alternative to distillation. Liquid–liquid extraction allows us to obtain high-standard ethanol. This also lowers the energy cost of the process in comparison to distillation (*1*). We are trying to find an adequate solvent for the extraction of the ethanol from the water mixtures; for this reason, in this research we have determined the equilibrium data of the aforesaid systems which have not been found in the literature.

Table I. Experimental and Literature Values for the Refractive Indexes at 293 K, n^{293}_D, of the Chemicals Used

chemical	exptl	ref *2*	ref *3*
ethyl alcohol	1.3610	1.3610	1.3611
hexanoic acid	1.4160	1.4163	1.4163
heptanoic acid	1.4218	1.4216	1.4170
octanoic acid	1.4278	1.4280	1.4285
nonanoic acid	1.4328	1.4330	1.4343
phthalic acid diethyl ester	1.5003	1.5049[a]	1.5000
phthalic acid dibutyl ester	1.4910	1.4900	1.4911
phthalic acid dioctyl ester	1.4864		1.4867

[a] Measured at 287 K.

Experimental Section

Chemicals. Twice distilled water, ethyl alcohol (Panreac 99.5%), hexanoic acid (Fluka 99.5%), heptanoic acid (Fluka 99%), octanoic acid (Fluka 99.6%), nonanoic acid (Fluka 97%), phthalic acid diethyl ester (Merck 99%), phthalic acid

0021-9568/88/1733-0468$01.50/0 © 1988 American Chemical Society