an equation given by Janz (*4*).

(2) For fixed $SrCl_2$ content in the melt, the addition of NaCl increases the conductivity. This effect is shown in Figure 4 for $X_{SrCl_2} = 0.3$. For increasing KCl content and fixed $SrCl_2$ composition, conductivity decreases rapidly at constant temperature. Again, higher temperature yields higher specific conductivity.

Discussion

The reliability of conductivity measurements reported in this study was checked by comparing κ values obtained at 973 K for the NaCl–KCl system with results by Matiašovsky et al. (*5*). Their value obtained for the equimolar NaCl–KCl mixture, 2.338 Ω^{-1} cm^{-1}, is in excellent agreement with the value obtained in the present study, 2.35 ± 0.01 Ω^{-1} cm^{-1}. Thus, one can assume that dependences observed in the ternary NaCl–KCl–$SrCl_2$ system can be trusted.

Keeping in mind that one is looking for a composition of a potential electrolyte, it should be assumed that $SrCl_2$ content in the salt mixture cannot be too high. The solubility of strontium in pure strontium chloride is high. At elevated temperatures it varies from about 6 mol % at monotectic temperature 1112 K (*6*) to about 25 mol % at the temperature 1273 K (*7*). There is a real danger that due to this phenomenon high $SrCl_2$ content in the electrolyte can affect efficiency of the process. At the same time, an increase of the $SrCl_2$ content decreases the conductivity. Thus, it is suggested for the above reasons that $X_{SrCl_2} = 0.3$ should not be exceeded.

The choice of the KCl/NaCl ratio at fixed X_{SrCl_2} depends on the choice between the temperature of the process and the conductivity of the electrolyte. The KCl–$SrCl_2$ phase diagram (*1*) indicates the existence of two double compounds, $2KCl\cdot SrCl_2$ and $KCl\cdot 2SrCl_2$. Their presence must correspond to the appearance of complex ions in the liquid, probably of the $SrCl_4^{-2}$ type. The resulting mobility of Sr^{2+} ions must fall, and the transference number, $t_{Sr^{2+}}$, must be very small. This kind of phenomenon was observed in the KCl–$MgCl_2$ solution (*8*). Thus, the rapid decrease of conductivity shown in Figure 4 for KCl-rich compositions may follow directly from complex ion formation. For this reason, the composition of the potential electrolyte should be located close to the limiting binary NaCl–$SrCl_2$ system, where the conductivity of the liquid electrolyte is higher. However, the temperature of the process may require the shift of the electrolyte composition toward the KCl-rich side, where the liquidus temperature is lower. This optimum must be found through further experimentation.

Registry No. NaCl, 7647-14-5; KCl, 7447-40-7; $SrCl_2$, 10476-85-4.

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Micellar Behavior of Praseodymium Valerate Dissolved in Binary Methanol and Benzene Mixtures

K. N. Mehrotra, Meera Sharma, and A. S. Gahlaut*

Department of Chemistry, Institute of Basic Sciences, Agra University, Khandari, Agra 282 002, India

Conductance results showed that praseodymium valerate behaves as a weak electrolyte in dilute solutions below the critical micelle concentration (cmc) and the cmc increases with increasing temperature. The various thermodynamic parameters were also evaluated for both dissociation and micellization processes. The viscosity data were interpreted in light of well-known equations. The ultrasonic velocities in the soap solutions were measured, and the results were used to evaluate thermodynamic and acoustic parameters. The results of cmc were found in excellent agreement with those obtained from other properties.

Introduction

Studies on the utilization of metallic soaps in various industries are still being carried out as the problem is of immense importance from pharmaceutical and technical points of view. The practical utility of these metal soaps has attracted the attention of several workers, as their physicochemical characteristics and structure largely depend on the conditions and methods of preparation. The survey of literature reveals that very few references are available on rare-earth metal soaps (*1–10*).

The micelle formation in a solvent depends upon its solubility parameter and ability to solvate the surfactant. The lower praseodymium soaps possess higher solubility in mixed solvents (methanol–benzene mixtures) rather than in pure solvents (methanol or benzene) and have been chosen to study the behavior of these soaps in such solvents. In this paper we report experimental conductivity, viscosity, and ultrasonic data for praseodymium valerate dissolved in binary mixtures containing benzene and methanol. Results of these measurements are used to calculate thermodynamic, interactional, and acoustical parameters.

Experimental Section

All the chemicals used were of BDH/AR grade. Praseodymium valerate was prepared by the direct methathesis of the corresponding potassium soap with the required amount of aqueous solution of praseodymium nitrate at 50–60 °C under

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* To whom correspondence should be addressed at the Department of Chemistry, Government College, Kanker, Baster (M.P.) 494 334, India

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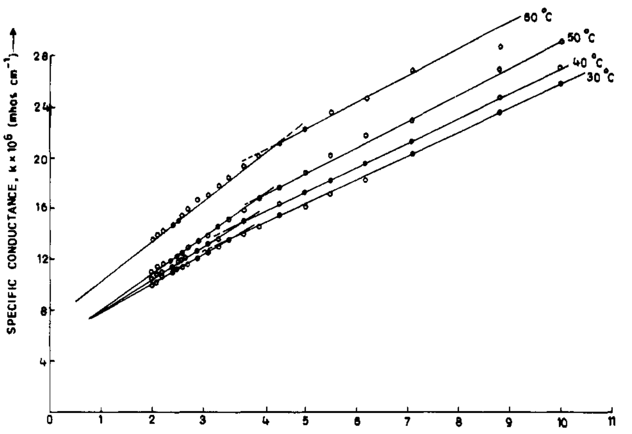

Figure 1. Specific conductance vs concentration of praseodymium valerate in a methanol-benzene mixture (50% v/v).

Table I. Cmc Values (g-mol L^{-1}) of Praseodymium Valerate

temp, °C	cmc × 10^3	temp, °C	cmc × 10^3
30	3.5	50	4.1
40	3.8	60	4.5

Table II. Degree of Dissociation of Prasoeydmium Valerate in a Methanol-Benzene Mixture (50% v/v) at Different Temperatures

		degree of dissociation			
S. no.	C^a	30 °C	40 °C	50 °C	60 °C
1	2.1	0.573	0.538	0.518	0.486
2	2.2	0.557	0.523	0.513	0.477
3	2.4	0.529	0.492	0.484	0.450
4	2.5	0.526	0.488	0.477	0.444
5	2.6	0.513	0.478	0.466	0.438
6	2.7	0.499	0.475	0.457	0.435
7	2.9	0.480	0.458	0.444	0.423
8	3.1	0.473	0.445	0.429	0.405
9	3.3	0.461	0.439	0.420	0.397
10	3.5	0.459	0.431	0.413	0.389
11	3.8	0.440	0.413	0.392	0.376
12	4.1	0.423	0.407	0.379	0.365
13	4.5	0.105	0.391	0.364	0.348
14	5.0	0.383	0.376	0.345	0.328
15	5.5	0.366	0.363	0.332	0.316
16	6.2	0.352	0.350	0.319	0.298
17	7.1	0.335	0.324	0.305	0.278
18	8.8	0.311	0.303	0.285	0.248
19	10.0	0.275	0.227	0.224	0.210

^{a} C = concentration.

Table III. Values of Limiting Molar Conductance μ_0 of Praseodymium Valerate at Different Temperatures

	μ_0			
% methanol	30 °C	40 °C	50 °C	60 °C
40	8.76	11.01	12.36	14.09
50	9.39	11.88	12.90	14.61
60	15.71	18.18	20.11	24.26

Table IV. Values of Dissociation Constant

	K_D × 10^8			
% methanol	30 °C	40 °C	50 °C	60 °C
40	25.1	12.0	6.0	3.4
50	35.3	15.1	7.6	3.8
60	48.7	19.9	9.3	4.3

vigorous stirring. The soap was purified by recrystallization, and the purity was checked by elemental analysis, mp determination, and IR spectra.

The solutions of praseodymium valerate were prepared by dissolving the required amount of soap in methanol-benzene mixtures of known compositions and were kept for 2 h in a thermostat at the desired constant temperature.

The conductance measurements of the solutions were performed with a Toshniwal digital conductivity meter Model CL 01.10A and dipping-type conductivity cell with platinized electrodes at a constant temperature. The specific conductance and molar conductance have been expressed in mhos cm^{-1} and mhos cm^{-1} g-mol^{-1} L, respectively. The viscosity measurements of the solutions of praseodymium valerate in a methanol-benzene mixture (50% v/v) were carried out by means of an Ostwald's Viscometer at constant temperature (40 ± 0.05 °C). The ultrasonic velocity was measured on a multifrequency ultrasonic interferometer (Model M-83, Mittal Enterprises, New Delhi, India) using a crystal of 6 MHz at a constant temperature (40 ± 0.05 °C). The uncertainty in the velocity results was 0.2%.

Results and Discussion

Conductivity. The specific conductance of the dilute solutions of praseodymium valerate in methanol-benzene mixtures of varying compositions (40%, 50%, and 60% methanol) increases with either increasing temperature, soap concentration, or methanol concentration. The plots of specific conductance vs soap concentration (Figure 1) are characterized by an intersection of two straight lines at a point that corresponds to the critical micelle concentration (cmc). The increase in temperature shifts the cmc to higher soap concentration, and the cmc was found to independent of solvent composition (Table I). This may be explained on the basis of the fact that at higher temperatures the electrostatic forces between the negative and positive ions decrease and thus favor the dissociation of the solute molecule, which ultimately favor the micellization. The values of cmc have also been determined for higher praseodymium soaps in 1-pentanol (*11*). It has been found that the cmc of these soaps decreases with increasing anion chain length in the soap molecule.

The molar conductance μ and degree of dissociation α of dilute solutions of praseodymium valerate decrease with increasing soap concentration and increase with the increase in the percentage of methanol in the solvent mixture. The values of molar conductance increase while the degree of dissociation decreases with increasing temperature (Table II). Nonlinear plots of molar conductance μ vs the square root of the soap concentration $C^{1/2}$ indicates that the soap behaves as a weak electrolyte and the Debye-Huckel-Onsager's equation is not applicable to these soap solutions. The limiting molar conductance μ_0 cannot be obtained by the usual extrapolation method. Since the soap behaves as a weak electrolyte in dilute solutions below the cmc, an expression for the dissociation can be developed in Ostwald's manner:

$$\underset{C(1-\alpha)}{(RCOO)_3Pr} \rightleftharpoons \underset{C\alpha}{Pr^{3+}} + \underset{3C\alpha}{3RCOO^-}$$

$$K_D = \frac{C\alpha(3C\alpha)^3}{C(1-\alpha)} = \frac{27C^3\alpha^4}{1-\alpha} \tag{1}$$

$$\Delta G_D{}^\circ = -RT \ln K_D \tag{2}$$

where α, K_D, and $\Delta G_D{}^\circ$ denote the degree of dissociation, the dissociation constant, and Gibbs free energy of dissociation, respectively. Since α is very small, the interionic effects may be treated as negligible. Thus, with consideration of α as conductance ratio μ/μ_0 and with rearrangement, eq 1 can be written as

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

Table V. Thermodynamic Parameters of the Dissociation Process at Different Temperatures

	$\Delta G_D°$, kJ mol^{-1}				$\Delta S_D° \times 10^2$, kJ K^{-1} mol^{-1}			
% methanol	30 °C	40 °C	50 °C	60 °C	30 °C	40 °C	50 °C	60 °C
40	12.75	13.82	14.88	15.86	22.19	21.82	21.47	21.12
50	12.47	13.62	14.67	15.76	24.32	23.91	23.50	23.12
60	12.20	13.38	14.49	15.65	26.76	26.28	25.81	25.39

Table VI. Thermodynamic Parameters of the Association Process at Different Temperatures

	$\Delta G_A°$, kJ mol^{-1}				$\Delta S_A° \times 10^2$, kJ K^{-1} mol^{-1}			
% methanol	30 °C	40 °C	50 °C	60 °C	30 °C	40 °C	50 °C	60 °C
40	42.54	43.52	44.50	45.36	18.21	17.94	17.69	17.42
50	42.99	43.97	44.97	45.85	18.36	18.08	17.83	17.56
60	43.40	44.41	45.42	46.31	18.49	18.22	17.97	17.70

Table VII. Density and Viscosity of Praseodymium Valerate in a Methanol–Benzene Mixture (50% v/v) at 40 ± 0.05 °C[a]

S. no.	$C \times 10^3$, g·mol L^{-1}	ρ, g mL^{-1}	η, cP	η_{sp}, cP	η_{sp}/C, cP/(g-mol L^{-1})	$\eta_{sp}/C^{1/2}$, cP/(g-mol L^{-1})$^{1/2}$	$(\eta/\eta_0)^2$	1/log (η/η_0)
1	1.0	0.8321	0.6311	0.0195	19.5	0.609	1.039	118.9
2	2.0	0.8429	0.6428	0.0384	19.2	0.853	1.078	61.0
3	3.0	0.8562	0.6540	0.0565	18.8	1.027	1.116	41.8
4	4.0	0.8678	0.6662	0.0762	19.0	1.209	1.158	31.3
5	5.0	0.8869	0.6879	0.1113	22.3	1.567	1.235	21.8
6	6.0	0.9090	0.7061	0.1407	23.4	1.827	1.301	17.5
7	7.0	0.9271	0.7280	0.1761	25.1	2.096	1.383	14.2
8	8.0	0.9488	0.7502	0.2119	26.5	2.381	1.469	11.9
9	9.0	0.9680	0.7679	0.2405	26.7	2.531	1.539	10.7
10	10.0	0.9872	0.7900	0.2762	27.6	2.762	1.629	9.4

[a] Abbreviations: C = concentration of soap, ρ = density, η = viscosity, and η_{sp} = specific viscosity.

The plots of μ^3C^3 vs $1/\mu$ are linear below the cmc. The dissociation constant K_D and molar conductance at infinite dilution μ_0 were evaluated from the slope ($K_D\mu_0^4/27$) and intercept ($-K_D\mu_0^3/27$) of the μ^3C^3 vs $1/\mu$ plots below the cmc and are recorded in Tables III and IV. The molar conducance at infinite dilution increases with increasing temperature and concentration of methanol in the solvent mixture. This may be due to the increasing charge on the micelle due to easier dissociation of soap molecules. The value of the dissociation constant increase with an increasing amount of methanol in the solvent mixture but decrease with increasing temperature. The decrease of the dissociation constant with increasing temperature indicates the exothermic nature of the dissociation process.

The values of the heat of dissociation for praseodymium valerate obtained from the linear plots of log K_D vs $1/T$ are -54.49, -61.24, and -68.89 kJ mol^{-1} for methanol–benzene mixtures containing 40%, 50%, and 60% methanol, respectively.

For the aggregation process, the standard free energy of micellization (per mole of monomer) $\Delta G_A°$, for the phase-separation model (*12*, *13*), is given by the relationship

$$\Delta G_A° = 2RT \ln x_{cmc} \tag{4}$$

where x_{cmc} is the cmc expressed as a mole fraction.

The free energy values of the dissociation $\Delta G_D°$ and micellization $\Delta G_A°$ have been calculated per mole of monomer and are recorded (Tables V and VI). The higher values of decrease in free energy for the micellization process than for the dissociation process favor micellization. The standard enthalpy change of micellization per mole of monomer for the phase-separation model (*12*, *13*) $\Delta H_A°$ is given by the relationship

$$\ln x_{cmc} = \frac{-\Delta H_A°}{2RT} + C \tag{5}$$

The values of $\Delta H_A°$ for praseodymium valerate have been obtained from the linear plot of $\ln x_{cmc}$ vs $1/T$ and found to be 12.64 kJ mol^{-1}. The positive value of $\Delta H_A°$ indicates that the association process of soap is endothermic. The results show that the association process is dominant over the dissociation process.

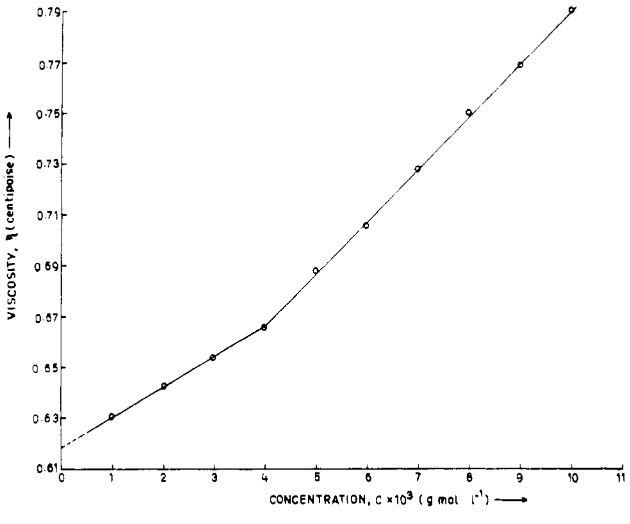

Figure 2. Viscosity vs concentration of praseodymium valerate in a methanol–benzene mixture (50% v/v) at 40 °C.

The standard entropy change for the dissociation and micellization processes $\Delta S_D°$ and $\Delta S_A°$ were evaluated with the expression

$$\Delta S° = \frac{\Delta H° - \Delta G°}{T} \tag{6}$$

The values of $\Delta S_D°$ and $\Delta S_A°$ for praseodymium valerate have been tabulated (Tables V and VI).

The values of the thermodynamic parameters showed that the association process is dominant over the dissociation process and that the dissociation of soap is exothermic while the association process is endothermic in nature.

***Viscosity*.** The viscosity η and specific viscosity η_{sp} of the dilute solutions of praseodymium valerate in a methanol–benzene mixture (50% v/v) increase with an increase in the soap concentration (Table VII), which may be due to the in-

Table VIII. Ultrasonic Velocity and Acoustic Parameters of Praseodymium Valerate in a Methanol–Benzene Mixture (50% v/v) at 40 ± 0.05 °C[a]

S. no.	$C \times 10^3$, g-mol P^{-1}	$\upsilon \times 10^{-5}$, cm S^{-1}	$\beta \times 10^{11}$, cm² dyn⁻¹	L_f, Å	$Z \times 10^{-5}$, cgs	$-\phi_k \times 10^6$, cm² dyn⁻¹	S_n
1	1.0	1.122	9.55	0.627	9.34	3.47	7.8
2	2.0	1.128	9.32	0.618	9.51	3.50	8.2
3	3.0	1.133	9.09	0.612	9.70	3.61	8.6
4	4.0	1.140	8.87	0.605	9.89	3.59	8.4
5	5.0	1.150	8.52	0.592	10.19	4.02	8.4
6	6.0	1.160	8.17	0.580	10.54	4.36	8.4
7	7.0	1.169	7.89	0.570	10.84	4.44	10.8
8	8.0	1.180	7.57	0.558	11.19	4.59	12.6
9	9.0	1.191	7.28	0.548	11.53	4.65	13.7
10	10.0	1.201	7.02	0.538	11.86	4.67	14.6

[a] Abbreviations: C = concentration of soap, υ = ultrasonic velocity, β = adiabatic compressibility, L_d = intermolecular free length, Z = specific acoustic impedance, ϕ_k = apparent molar compressibility, and S_n = solvation number.

creasing tendency of the soap molecules to form aggregation at higher soap concentration. The plots of viscosity η vs soap concentration (Figure 2) are characterized by an intersection of two straight lines at a definite soap concentration, which corresponds to the cmc (4×10^{-3} M) of the soap.

The viscosity results have been explained in light of equations proposed by Einstein (*14*), Vand (*15*), Moulik (*16*), and Jones-Dole (*17*). The values of molar volume $\bar{V}$ of the soap calculated from the slope of Einstein's plot (η_{sp} vs C) and Vand's plot ($1/C$ vs $1/\log(\eta/\eta_0)$) below the cmc are 7.6 and 6.4 L mol⁻¹, respectively.

The plots of Moulik's equation ($(\eta/\eta_0)^2$ vs C^2) and Jones-Dole's equation ($\eta_{sp}/C^{1/2}$ vs $C^{1/2}$) are characterized by a break at the cmc. The values of Moulik's constants M and K have been calculated from the intercept and slope of the plot and are found to be 1.052 and 7×10^3, respectively.

The values of the constants ($A = 0$ and $B = 18$) of the Jones–Dole equation have been calculated from the intercept and slope of the plot below the cmc. The higher value of constant B (soap–solvent interaction) as compared to that of constant A (soap–soap interaction) confirms that the soap molecules do not aggregate appreciably below the cmc and there is a sudden change in the aggregation at the cmc.

It is, therefore, concluded that the viscosity results can be explained in light of various well-known equations. The values of the cmc and molar volume indicate the applicability of both these equations.

Ultrasonic Data. The ultrasonic velocity of the solutions of praseodymium valerate increases with increasing soap concentration (Table VIII). The variation of velocity with soap concentration depends upon the concentration derivatives of ρ and β:

$$\frac{dv}{dc} = -\frac{v}{2}\left[\frac{1}{\rho}\frac{d\rho}{dc} + \frac{1}{\beta}\frac{d\beta}{dc}\right] \tag{7}$$

The results (Table VII) indicate that the density increases whereas the adiabatic compressibility decreases with increasing soap concentration. The variation of ultrasonic velocity with concentration is in fair agreement with the results of other workers (*18–20*).

The plots of ultrasonic velocity v vs soap concentrations C (Figure 3) and adiabatic compressibility B, intermolecular free length L_f, and specific acoustic impedance Z vs soap concentration C are characterized by an intersection of two straight lines at a point that corresponds to the cmc of the soaps (4.0×10^{-3} M).

The adiabatic compressibility of dilute solutions of praseodymium valerate decreased with the increase in the soap concentration. This decrease may be due to the orientation of solvent molecules around the ions and results in increasing the internal pressure and lowering the compressibility of the solutions.

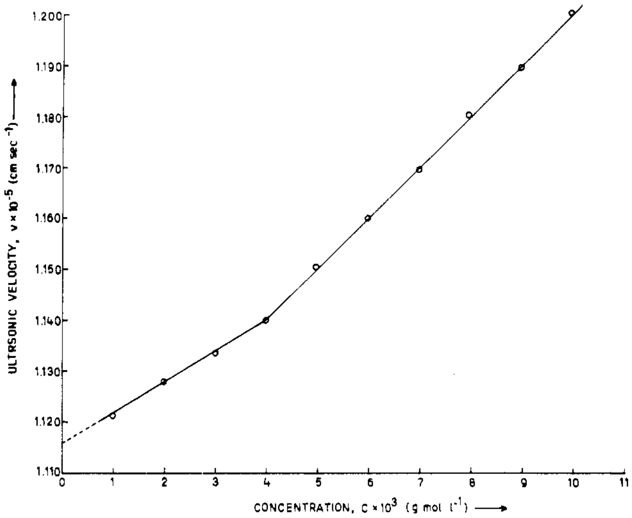

Figure 3. Ultrasonic velocity vs concentration of praseodymium valerate in a methanol–benzene mixture (50% v/v) at 40 °C.

The adiabatic compressibility β is found to obey Bachem's relationship (*21*):

$$\beta = \beta_0 + AC + BC^{3/2} \tag{8}$$

where β_0 is the compressibility of the solvent. The values of constants A and B have been obtained from the intercept and slope of the linear plot of $(\beta - \beta_0)/C$ vs $C^{1/2}$ and found to be 0.89×10^{-10} and 1.0×10^{-10}, respectively.

The decrease in the intermolecular free length ($L_f = K\beta^{1/2}$, where K is the temperature-dependent Jacobson's (*22*) constant) with increasing ultrasonic velocity indicates that there is a significant soap–solvent (*23*) interaction due to which the structural arrangement is considerably affected. The values of specific acoustic impedance (*24*) ($Z = \rho v$) increase with increasing soap concentration.

The apparent molal compressibility ϕ_k of a solution containing 1 mol of solute is given by the relationship

$$\phi_k = \frac{1000}{C\rho_0}(\rho_0\beta - \beta_0\rho) + \frac{M_2\beta_0}{\rho_0} \tag{9}$$

where M_2 is the molecular weight of the soap.

The values of the apparent molal compressibility decrease with increasing soap concentration.

Pasynskii (*25*) defined solvation number S_n as the number of solvent molecules present in the primary solvation sheath, which is given by the relationship

$$S_n = \frac{n_1}{n_2}\left(1 - \frac{V\beta}{n_1 V_0 \beta_0}\right) \tag{10}$$

where V is the volume of solution containing n_2 molecules of soap and V_0 is the molar volume of solvent. The results show that the solvation number increases with the increase of the concentration of soap. These results are in agreement with the results of other workers (*26-28*) reported for electrolytic solutions.

It is, therefore, concluded that the praseodymium valerate in a methanol-benzene mixture behaves as a weak electrolyte in dilute solutions below the cmc. The results show that there is a significant soap-solvent interaction in solution.

Registry No. Praseodymium valerate, 26176-68-1; benzene, 71-43-2; methanol, 67-56-1.

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Molar Excess Enthalpy for the Binary Systems 1,3-Dioxolane + 1,2-*trans*-Dichloroethylene, Tetrachloroethylene, or 1,1,2,2-Tetrachloroethane

Fabio Comelli

Centro di Studio per la Fisica delle Macromolecole del CNR, via Selmi 2, 40126 Bologna, Italy

Romolo Francesconi*

Dipartimento di Chimica "G. Ciamician", Università degli Studi, via Selmi 2, 40126 Bologna, Italy

Molar excess enthalpy (liquid-phase enthalpy of mixing) for 1,3-dioxolane + 1,2-*trans*-dichloroethylene, + tetrachloroethylene, or + 1,1,2,2-tetrachloroethane binary systems is determined at atmospheric pressure and at 298.15 K. The experimental data were correlated by means of the Redlich-Kister expression, and the adjustable parameters were evaluated by the least-squares method. The cell model and the quasichemical approximation of the lattice theory of solutions were tested. Associations were inferred only for the 1,3-dioxolane + 1,2-*trans*-dichloroethylene system.

Introduction

The present work is a part of a long-term study of the molar excess enthalpy H^E of binary systems containing 1,3-dioxolane as common solvent (component 1). The main purpose of these investigations is to study the dependence of H^E on the substituted groups of the second component and to find a connection between the chemical structure of the compounds and their properties.

The cell model and the quasichemical approximation of the lattice theory of solutions have been tested to confirm the possible presence of associations for the systems in question.

Chemicals

1,3-Dioxolane (D; a Fluka product, purum, analytical grade 99%) was purified by refluxing for about 10 h on Na wires in N flow, excluding moisture, and then fractionated on a Vigreux column (*1*).

1,2-*trans*-Dichloroethylene (DCE; an Aldrich product, analytical grade 98%) was further separated from the residual cis isomer contained in the commerical mixture by fractional distillation (Widmar 30-plate column) over a 10% aqueous sodium hydroxide solution until the density was constant.

Tetrachloroethylene and 1,1,2,2-tetrachloroethane (TCE and TCA, respectively; C. Erba products, analytical grade 99.5% and 98.5%, respectively) were washed over an anhydrous solid, calcium sulfate, and distilled for 10 h.

All purified compounds were stored in dark bottles and preserved over molecular sieves type 3A (C. Erba).

Experimental Section

Density Measurements of Pure Components. Table I shows the experimental data of density ρ of pure liquids, which are necessary to evaluate fluxes and hence mole fractions in the calorimetric measurements. These values were determined with a two capillary glass pycnometer (volume, 31.41 mL at 298.15 K) calibrated with distilled mercury.

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