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Excess Viscosities of Binary Mixtures of Chloroform and Alcohols

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Viscosities of mixtures of chloroform with methanol, ethanol, and 1-propanol were measured at 30, 38, and 46 °C. At least 5 mole fractions, covering the range, were studied for each liquid pair. Excess viscosities show the interesting result of being positive at some mole fractions and negative at other mole fractions.

Introduction

The heat of mixing of most binary pairs of liquids either is exothermic throughout the entire range of mole fractions or is endothermic for all mole fractions. Mixtures of chloroform and alcohols are unusual, in that ΔH_{mix} is negative when the mole fraction of chloroform is small and positive when the mole fraction of chloroform is large (*1–4*).

Other properties of these systems also exhibit interesting behavior. The volumes of mixing of solutions of chloroform with either ethanol or 1-propanol also undergo a sign change as mole fraction is varied (*5*). This behavior is consistent with the enthalpy measurements, in that ΔV_{mix} is positive over approximately the same mole fraction range that ΔH_{mix} is positive. Both of these quantities have been interpreted in terms of the relative magnitude of the interactions between molecules in the two pure liquids compared with the interactions in the mixture (*6*). On the other hand, the $CHCl_3$-CH_3OH system exhibits a volume of mixing that is negative for all mole fractions (*5*).

Both methanol and ethanol have a minimum boiling azeotrope with chloroform (*7*). Such azeotropes generally mean that the forces between unlike molecules in the binary pair are weak compared with forces between like molecules (*8*). This is consistent with endothermic mixing, but not with exothermic mixing.

Viscosity also depends on the magnitude of interactions in a fluid. Thus, as part of our research program in viscosity measurements (*9*), we have undertaken a study of the viscosities of these interesting systems in an attempt to better understand the reasons for their unusual behavior.

Experimental Section

Reagent-grade chloroform, methanol, and 1-propanol were purified by simple distillation. Anhydrous ethanol was kept dry by storage over no. 4 molecular sieves.

Flow times were measured to 100th of a second by using a Schott Gerate AVS 300 viscosity measuring unit. The Ubbelohde viscometer tubes were calibrated with use of doubly deionized water. Temperatures were maintained to ±0.02 °C with a Schott Gerate CT050 temperature controller.

Table I. Viscosities and Densities of Mixtures of Chloroform and Alcohols at 303, 311, and 319 K

	303 K		311 K		319 K	
$X_{\mathrm{CHCl_3}}$	d, g/mL	η, cP	d, g/mL	η, cP	d, g/mL	η, cP
			Methanol			
0.0000	0.7835	0.5126	0.7763	0.4603	0.7608	0.4116
0.0960	0.9018	0.5644	0.8925	0.5043	0.8836	0.4586
0.1963	1.0177	0.6289	1.0060	0.5549	0.9949	0.4932
0.2971	1.1018	0.6315	1.0883	0.5593	1.0783	0.5022
0.4963	1.2380	0.5872	1.2247	0.5271	1.2120	0.4779
0.6952	1.3441	0.5447	1.3296	0.4971	1.3151	0.4574
0.9092	1.4321	0.5211	1.4168	0.4822	1.4010	0.4489
1.0000	1.4628	0.5249	1.4472	0.4893	1.4315	0.4571
			Ethanol			
0.0000	0.7813	0.9817	0.7743	0.8481	0.7672	0.7348
0.1074	0.8718	0.9539	0.8626	0.8217	0.8536	0.7107
0.2892					1.0034	0.6097
0.2992	1.0352	0.8095	1.0209	0.7021		
0.5029	1.1766	0.6591	1.1593	0.5849	1.1457	0.5234
0.6978	1.3016	0.5679	1.2875	0.5169	1.2715	0.4922
0.9003	1.4120	0.5256	1.3969	0.4864	1.3817	0.4517
1.0000	1.4638	0.5254	1.4485	0.4893	1.4330	0.4566
			1-Propanol			
0.0000	0.7979	1.7229	0.7913	1.4295	0.7851	1.1971
0.0987	0.8676	1.5382	0.8600	1.2831	0.8518	1.0802
0.2941					0.9818	0.8178
0.2987	1.0079	1.0650	0.9957	0.9064		
0.4970					1.1175	0.6404
0.4992	1.1400	0.8162	1.1295	0.7227		
0.6990	1.2707	0.6346	1.2567	0.5734	1.2406	0.5202
0.9085	1.4035	0.5383	1.3889	0.4977	1.3730	0.4655
1.0000	1.4628	0.5249	1.4472	0.4893	1.4315	0.4571

Table II. Literature Values of Viscosities (cP) of Pure Alcohols at 30 °C

ref	CH_3OH	C_2H_5OH	C_3H_7OH
10	0.513	0.994	1.728
this work	0.5126	0.9817	1.7229
11[a]	0.5091	0.9628	1.6517

[a] Data from ref 11 fit by least-squares to give the following equations: CH_3OH, $\ln \eta = 1247.6(1/T) - 4.7928$ ($r = 0.9999$); C_2H_5OH, $\ln \eta = 1667.3(1/T) - 5.5406$ ($r = 0.9999$); nC_3H_7OH $\ln \eta = 2022.1(1/T) - 6.1721$ ($r = 0.9978$).

Densities were determined to ±0.0002 g/cm^3 by using a Mettler Parr DMA 45 digital density meter, calibrated with water at each temperature. Temperature was controlled to ±0.01

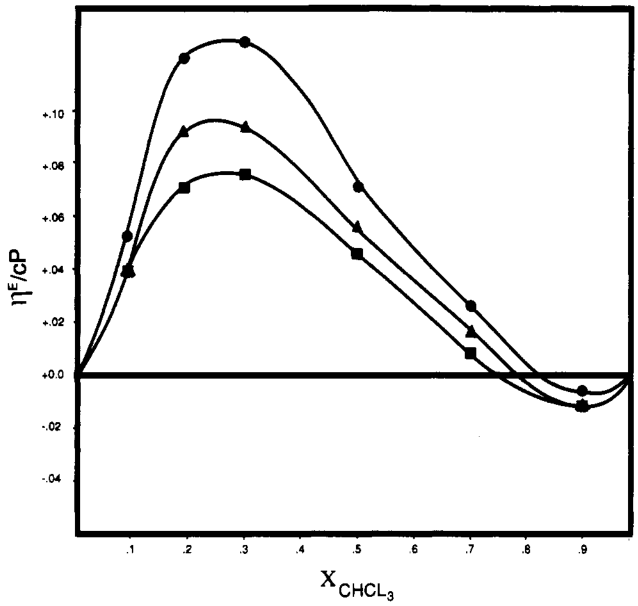

Figure 1. Excess viscosities (cP) of mixtures of chloroform and methanol at 30 °C (●), 38 °C (▲), and 46 °C (■).

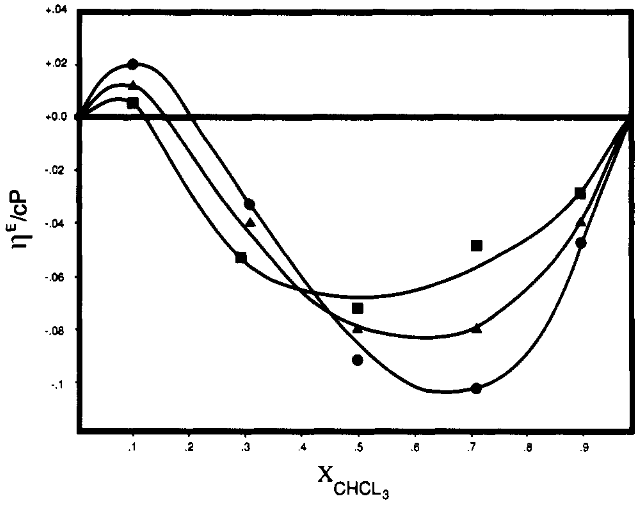

Figure 2. Excess viscosities (cP) of mixtures of chloroform and ethanol at 30 °C (●), 38 °C (▲), and 46 °C (■).

°C by a Neslab RTE 5DD digital refrigerator bath. Values measured for the pure alcohols are within 0.2% of literature values (*10*).

Results

The viscosities of the alcohol-chloroform mixtures are given as a function of mole fraction for all three temperatures in Table I. As shown in Table II, the values for the pure alcohols are in agreement with literature results (*10*, *11*). Similarly, our value for the viscosity of pure chloroform falls between those found in the literature (*12*, *13*). Viscosities for the chloroform-methanol system have been reported at 25 °C (*12*). In all cases, our viscosity values at 30 °C are slightly lower than the values previously measured at comparable mole fractions at 25 °C.

Values of the excess viscosity, given by eq 1, are shown in Table III and graphed in Figures 1-3.

$$\eta^E = \eta - X_{CHCl_3}\eta_{CHCl_3} - (1 - X_{CHCl_3})\eta_{ROH} \qquad (1)$$

The excess viscosity shows a clear trend. Values for the methanol-chloroform pair are mainly positive, with that of mole fraction X_{CHCl_3} = 0.909 being slightly negative. The excess viscosity for ethanol-chloroform is positive only for X_{CHCl_3} = 0.107. All excess viscosity values for the 1-propanol-chloroform system are negative.

Table III. Excess Viscosities of Mixtures of Chloroform and Alcohols at 303, 311, and 319 K

X_{CHCl_3}	η^E_{303}	η^E_{311}	η^E_{319}
	Methanol		
0.0960	+0.0506	+0.0412	+0.0426
0.1963	+0.1139	+0.0889	+0.0727
0.2971	+0.1152	+0.0904	+0.0771
0.4963	+0.0685	+0.0524	+0.0437
0.6952	+0.0235	+0.0166	+0.0142
0.9092	−0.0027	−0.0045	−0.0041
	Ethanol		
0.1074	+0.0213	+0.0121	+0.0058
0.2892			−0.0446
0.2992	−0.0355	−0.0387	
0.5029	−0.0929	−0.0828	−0.0715
0.6978	−0.0950	−0.0808	−0.0485
0.9003	−0.0448	−0.0387	−0.0326
	1-Propanol		
0.0987	−0.0665	−0.0536	−0.0439
0.2941			−0.1616
0.2987	−0.3000	−0.2422	
0.4970			−0.1889
0.4992	−0.3086	−0.2374	
0.6990	−0.2509	−0.1989	−0.1597
0.9085	−0.0962	−0.0776	−0.0593

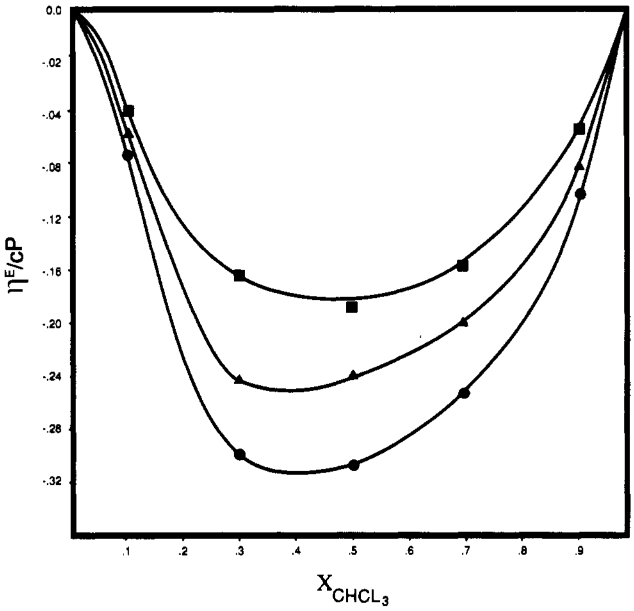

Figure 3. Excess viscosities (cP) of mixtures of chloroform and 1-propanol at 30 °C (●), 38 °C (▲), and 46 °C (■).

Discussion

In the region of large mole fraction of chloroform, the endothermic heat of mixing has been explained as being due to the breaking of the hydrogen bonds between the few alcohol molecules as they disperse throughout the chloroform (*3*, *4*). This endothermic effect outweighs the exothermic formation of the alcohol-chloroform interactions. A positive ΔH_{mix} suggests that the overall amount of interaction has diminished upon mixing. This should result in a negative excess viscosity. All three systems do show η^E to be negative in the high mole fraction of chloroform region. The methanol system is just barely negative; ethanol is more so, with a minimum η^E of −0.1 cP; 1-propanol has the most negative η^E (−0.3 cP).

In the low mole fraction of chloroform region, the exothermic heat of mixing values are due to formation of ROH-CHCl$_3$ interactions. This can occur without disrupting the alcohol hydrogen bonds since only relatively few $CHCl_3$ molecules are present (*3*, *4*). The net increase in interaction that results should cause η^E to be positive. This does occur for the methanol-chloroform system, which shows η^E to be mainly positive with a maximum value of +0.1 cP. It also occurs to a lesser extent for ethanol (η^E_{max} = +0.02 cP).

The 1-propanol system never exhibits a positive excess viscosity. Apparently the longer alkyl chain diminishes the chloroform-alcohol interactions enough that all η^E are negative. Thus, it is likely that higher straight-chain alcohols will all exhibit negative excess viscosities throughout the entire range of compositions.

The effect of a temperature increase is, in all cases, to break interactions and permit easier flow. This tends to diminish differences between solutions. The result is low absolute values of η^E at higher temperatures. This can be seen in all three of the figures. It is particularly striking in the case of ethanol-chloroform. Figure 2 exhibits a crossover point at $X_{CHCl_3} \sim 0.4$. The high-temperature η^E values are less positive and less negative.

Glossary

d	density (g/mL)
ΔH_{mix}	enthalpy of mixing
ΔV_{mix}	volume of mixing
η	viscosity (cP) of a mixture
η^E	excess viscosity (cP) as defined in eq 1
X_{CHCl_3}	mole fraction of chloroform

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Temperature and Concentration Dependence of Electrical Conductance of a Mixture of Sodium and Potassium Thiocyanates in Aqueous Medium

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Molar conductance and density of the [xNaSCN + (1 - x)KSCN] + RH_2O system were measured as functions of x, R, and temperature (283-323 K). Deviation of molar conductance from additivity occurs at all the temperatures in the region $R \leq 10$. The amount of this deviation is found to be independent of temperature. The isothermal concentration dependence of molar conductance was described by the expression $\Lambda = \Lambda_{FLK} \exp(Bc + Cc^2)$, where Λ_{FLK} is the Falkenhagen-Leist-Kelbg equation for Λ. B and C are empirical constants, and c is the molar concentration. The temperature dependence of Λ has been described by the Vogel-Tammann-Fulcher equation.

Introduction

Data on the transport properties of mixed electrolytes in the aqueous medium are scarce in the literature. Recently, we reported (*1*) the electrical conductance of the [xNaSCN + (1 - x)KSCN] + RH_2O system as functions of x and R at 298 K. Deviation of molar conductance from additivity known as the mixed-alkali-metal effect was observed in this system in the region where $R \leq 10$. Reported here are the molar conductance and density values of this mixed electrolytic system at various other temperatures, from 283 to 323 K.

Experimental Section

Molal solutions were prepared by using recrystallized NaSCN (SD, reagent grade) and KSCN (SD, reagent grade). Conductivity measurements were made at 1 kHz with use of the CDM83 conductivity meter (Radiometer, Copenhagen) and a dip-type CDC304 conductivity cell. This cell has three electrodes in the form of pure platinum bands on a glass tube. Densities of the solutions were measured by using a calibrated glass pycnometer of about 7-cm^3 capacity. All measurements were made in a thermostated (±0.02 °C) water bath.

Results and Discussion

The experimental values of molar conductance, Λ, of the [xNaSCN + (1 - x)KSCN] + RH_2O system as functions of x, R, and temperature are presented in Table I. The density data are presented as a linear function of temperature in Table II. In order to examine the occurrence of deviation of Λ from additivity, the r factor, defined as $r = \Lambda_{add}/\Lambda$, is plotted against R in Figure 1 for x = 0.5. Λ_{add} is the molar conductance of the mixture of thiocyanates calculated by using the additivity principle. It is apparent from Figure 1 that at all the experimental temperatures significant deviation of Λ from additivity occurs around $R \leq 10$ only. The amount of deviation is also found to be almost independent of temperature in the range from 283 to 323 K, as evident from Figures 2 and 3.

Earlier we reported (*1*) a new semiempirical equation to describe the isothermal concentration dependence of Λ, which is of the form

$$\Lambda = \Lambda_{FLK} \exp(Bm + Cm^2) \quad (1)$$

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