J. Chem. Eng. Data 1990, 35, 6-8

Surface Tension of Refrigerants R123 and R134a

Hee Baik Chae,[†] James W. Schmidt,[*] and Michael R. Moldover

Thermophysics Division, National Institute of Standards and Technology (formerly National Bureau of Standards), Gaithersburg, Maryland 20899

The surface tensions of two environmentally acceptable refrigerants (R123, 2,2-dichloro-1,1,1-trifluoroethane; and R134a, 1,1,1,2-tetrafluoroethane) were measured with a differential capillary rise technique. Measurements span the temperature range −25 to +140 °C for R123 and −10 to +95 °C for R134a.

I. Introduction

In the near future, the production of certain fully halogenated chlorofluorocarbon (CFC) refrigerants will be phased out. There are very promising fluids that may serve as substitutes, either as pure fluids or as constituents of mixtures, or both. In particular, R123 (CCl_2HCF_3) and R134a (CF_3CFH_2) have emerged as leading candidates to replace R11 and R12, respectively, and are under active worldwide development by a number of chemical manufacturers.

Surface tension is a fluid property required to correlate and predict heat transfer when a phase change occurs. Surface tension influences the growth of bubbles in nucleate boiling and the drainage of condensate from condenser surfaces. In the following, we describe accurate surface tension measurements of two refrigerants R123 and R134a.

II. Measurements

The surface tensions of R123 and R134a were deduced from our measurements of the capillary length and the density measurements of Morrison and Ward (*1*). The capillary length parameter is

$$a^2 \equiv 2\sigma/(\rho_l - \rho_v)g \qquad (1)$$

Here, σ is the surface tension; ρ_l and ρ_v are the densities of the liquid and vapor, respectively; and g is the acceleration due to gravity 9.80 m/s^2. The capillary length can be determined from a relation derived by Rayleigh (*2*):

$$a^2 = r_i\left[h_i - h_0 + \frac{r_i}{3} - 0.1288\frac{r_i^2}{h_i - h_0} + 0.1312\frac{r_i^3}{(h_i - h_0)^2}\right] \qquad (2)$$

Here, r_i is the radius of capillary, i, and $h_i - h_0$ is the height of the meniscus in the ith capillary (h_i) above the bulk meniscus (h_0). The liquid–glass contact angle appeared by direct observation to be zero at ambient temperatures. The contact angle was assumed to be zero at other temperatures as well. We have used a differential capillary rise technique that avoids the difficult measurement of the location of the bulk meniscus h_0. h_i and h_j were measured for two different capillaries (r_i and r_j) in the same cell at each temperature. Then, eq 2 was written twice (once for each measurement). h_0 was numerically eliminated from the equations to determine a^2.

The sample cell contained four capillaries of the following bore radii: r_1 = 0.574 ± 0.001 mm, r_2 = 0.320 ± 0.001 mm, r_3 = 0.276 ± 0.002 mm, and r_4 = 0.148 ± 0.002 mm. Their radii were determined by partially filling the capillaries with plugs of mercury. The plugs were weighed and their lengths were measured with a traveling microscope. This procedure was repeated three times for each capillary.

Table I. Capillary Lengths for R123

T/°C	a_{12}^2/mm^2	a_{34}^2/mm^2
−25.66	2.759	
−10.62	2.607	
1.52	2.455	
10.14	2.347	
19.37	2.215	
30.50	2.067	
42.02	1.937	
50.83	1.821	
60.45	1.719	
70.06	1.571	
80.18	1.450	
90.29	1.298	
100.21	1.165	1.201
111.13	1.041	1.068
121.14	0.897	0.926
130.76	0.758	0.791
140.27	0.613	0.664

The capillaries were placed in a small pressure cell comprised of a thick-walled glass tube clamped between stainless steel plates and sealed with indium. A stainless steel valve was welded to one end plate of the cell. For each refrigerant, the cell was filled and evacuated several times before the final filling. The cell was placed in a thermostated bath (±0.02 K) with transparent windows. The capillary rise h_i was measured (±0.01 mm) for each capillary with a cathetometer.

R123 was obtained from Halocarbon Laboratories Inc. The manufacturer states that its purity was 99.95%. Its water content was found to be 0.003% via Karl Fischer titration. With the aid of gas chromatography and mass spectroscopy, it was found that the sample was comprised of 99.95% R123 and trace amounts of the thermodynamically similar isomer R123a. The R134a was obtained from the Du Pont Co. The manufacturer stated that its purity was 99.95%. The water content was found to be 0.005%. No significant halocarbon impurities were found in it. We used both samples without purification.

III. Results

We determined a^2 using eq 2 and measurements from two pairs of capillaries $a_{12}^2(r_1,r_2)$ and $a_{34}^2(r_3,r_4)$. The values for a_{12}^2 and a_{34}^2 are listed in Tables I and II. These values of a^2 were fitted to the functional form

$$a^2 = a_0^2 t^{0.935} \qquad (3)$$

where t is the reduced temperature $(T_c - T)/T_c$ and T_c is the critical temperature. In this expression, we used the values T_c = 456.94 K for R123 (*3*) and T_c = 374.205 K for R134a (*1*). These values were recently measured with samples taken from the same containers that we used. In eq 3, the exponent 0.935 is a theoretical value that is expected to apply very close to T_c (*4*). We used this value for the entire temperature range; thus, a single parameter, a_0^2, was fitted to the data for each refrigerant. We found a_0^2 = 5.79 and 6.35 mm^2 for R123 and R134a, respectively. The measured values of a^2 and the fitted

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[*] Person to whom correspondence should be addressed.

[†] Current address: Korea Standards Research Institute, Taejŏn, Korea.

Table II. Capillary Lengths for R134a

T/°C	a_{12}^2/mm^2	a_{34}^2/mm^2
-10.32	2.103	
-6.60	2.002	
0.92	1.862	
1.92	1.810	
2.62	1.807	
4.68	1.755	
5.63	1.772	
9.74	1.697	
19.57	1.500	
26.79	1.394	1.413
26.79		1.414
30.20	1.320	
30.20	1.329	
40.13	1.140	1.186
50.06	0.974	1.004
60.30	0.808	0.808
60.30	0.804	0.809
70.49		0.613
80.27		0.438
90.87		0.228
90.87		0.227
94.33		0.150
94.33		0.148
95.96		0.105

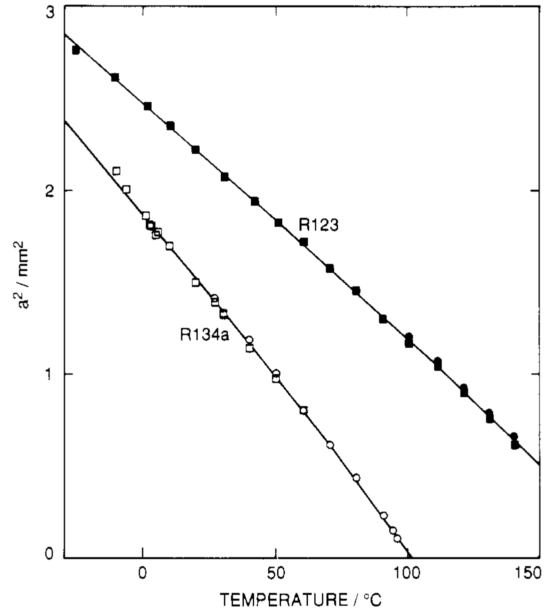

Figure 1. Capillary length squared vs temperature for refrigerants R123 and R134a. Data represented by squares were obtained from capillaries 1 and 2. Data represented by circles were obtained from capillaries 3 and 4. Solid symbols represent R123; open symbols represent R134a. Solid lines represent fits to eq 3.

curves are shown in Figure 1. The deviations ($a_{\mathrm{expt}}^2 - a_{\mathrm{calc}}^2$) are shown in Figure 2. As can be seen in Figures 1 and 2, eq 3 fits the data within the precision of the measurements.

The surface tensions σ were obtained from eq 1 with values of $\rho_l - \rho_v$ from the functional equation used by Morrison and Ward (*1*), and McLinden et al. (*5*), and the values of a^2 obtained from fitting eq 3. The values of σ are listed at 10 K intervals in Table III together with the values for ρ_v and ρ_l obtained from eqs 37 and 40 of McLinden et al. (*5*).

One can use the equation

$$\sigma = \sigma_0 t^{1.26} \tag{4}$$

with a single parameter σ_0 used to describe the surface tension. For R123, we found σ_0 = 58.1 mN/m, and for R134a, σ_0 = 60.8 mN/m. With these parameters, eq 4 agrees with the tabulated values of σ within 0.15 mN/m over the range of temperatures listed.

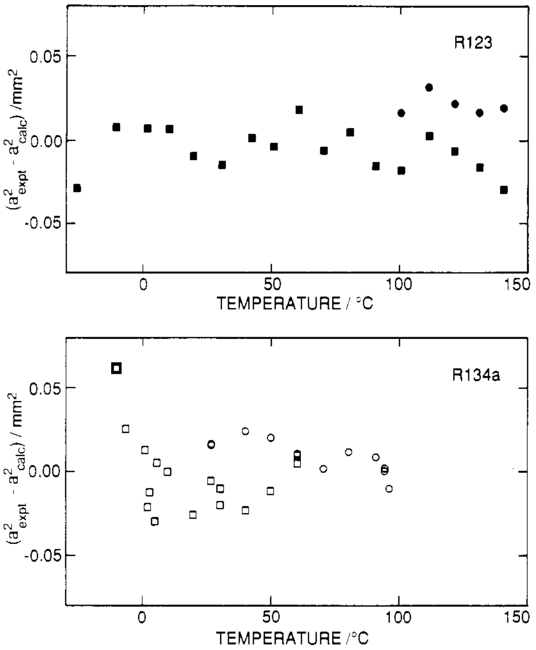

Figure 2. Deviations of the experimental points from the fit to eq 3 for R123 (upper plot) and R134a (lower plot). Squares and circles represent the same data as in Figure 1.

Table III. Surface Tensions

	R123			R134a		
T/C	ρ_l/ (kg/m^3)	ρ_v/ (kg/m^3)	σ/ (mN/m)	ρ_l/ (kg/m^3)	ρ_v/ (kg/m^3)	σ/ (mN/m)
-20	1572	0.9	20.94	1355	6.8	14.62
-10	1549	1.4	19.68	1324	10.0	13.15
0	1525	2.2	18.44	1292	14.4	11.71
10	1502	3.4	17.21	1259	20.3	10.30
20	1477	4.9	16.00	1224	27.8	8.92
30	1452	6.9	14.80	1187	37.5	7.58
40	1426	9.6	13.62	1147	50.0	6.28
50	1399	13.0	12.46	1103	66.2	5.02
60	1371	17.3	11.32	1055	87.2	3.82
70	1342	22.6	10.20	1000	115.5	2.69
80	1312	29.2	9.10	932	155.2	1.64
90	1280	37.3	8.02	842	216.0	0.72
100	1247	47.1	6.97	651	357.4	0.04
110	1212	59.0	5.94			
120	1174	73.6	4.95			
130	1132	91.6	3.99			
140	1087	114.0	3.08			
150	1036	142.1	2.22			

Acknowledgment

We acknowledge frequent and very helpful discussions with G. Morrison, L. Weber, A. Goodwin, and I. Pegg. We thank Sam Margolis and Tom Bruno for analyzing the refrigerants.

Glossary

a	capillary length, m
a_0	capillary length amplitude, m
σ	surface tension, N/m
σ_0	surface tension amplitude, N/m
ρ_l	liquid density, kg/m^3
ρ_v	vapor density, kg/m^3
g	acceleration due to gravity, 9.80 m/s^2
r_i	capillary radius, m
h_i	capillary rise, m
h_0	reference meniscus height, m
T	temperature, K
T_c	critical temperature (IPTS-68), K
t	reduced temperature, dimensionless

Registry No. (CCl_2HCF_3), 306-83-2; (CF_3CFH_2), 811-97-2.

Literature Cited

(1) Morrison, G.; Ward, D. To be submitted for publication in *Int. J. Thermophys*.
(2) Rayleigh, O. M. *Proc. R. Soc. London, Ser. A*. **1916**, *92*, 184.
(3) Weber, L.; Levelt-Sengers, J. To be published in *Fluid Phase Equilib*.
(4) Chaar, H.; Moldover, M. R.; Schmidt, J. W. *J. Chem. Phys*. **1986**, *85*, 418.
(5) McLinden, M. O.; Gallagher, J. S.; Weber, L. A.; Morrison, G.; Ward, D.; Goodwin, A. R. H.; Moldover, M. R.; Schmidt, J. W.; Chae, H. B.; Bruno, T. J.; Ely, J. F.; Huber, M. L. *ASHRAE Trans*., in press.

Received for review March 16, 1989. Accepted October 2, 1989. This work has been supported in part by NASA under Contract No. H-27954-B.

Thermodynamics of Transfer of Hydrogen Halides (HCl, HBr) in Glycerol–Dimethylformamide Mixtures from Electromotive Force Measurements

D. Muralimohan Rao and C. Kalidas*

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

The standard potentials of Ag–AgX (X = Cl^- or Br^-) electrodes in glycerol–dimethylformamide (Gly–DMF) mixtures in different solvent compositions (up to 60 wt % DMF for Ag–AgCl and 40 wt % DMF for Ag–AgBr electrodes) have been determined at three different temperatures from 25–35 °C by emf measurements with the cell Pt,H_2 (g, 1 atm)|HCl (*m*),DMF(x)–Gly(y)|AgX–Ag. The primary medium effects and the mean molal activity coefficients in the concentration ranges 0.01–0.02 mol kg^{-1} at 25 °C have been evaluated. The standard molal potentials, ${}_{s}E^{\circ}{}_{m}$, have been expressed as a function of temperature. The thermodynamic parameters for the transfer of HCl and HBr from glycerol to glycerol–DMF mixtures have been evaluated from emf data at 25 °C on the mole fraction scale. The significance of the various thermodynamic quantities associated with the transfer process is discussed.

Introduction

The thermodynamics of transfer of hydrogen halides in mixed and nonaqueous solvents in cells without liquid junctions has received considerable attention in recent years. The results have been mainly interpreted in terms of ion–solvent and solvent–solvent interactions by using suitable extrathermodynamic assumptions. Most of the data available in the literature from experiments employing Ag–AgCl and Ag–AgBr electrodes has been confined to mixed amphiprotic solvents (*1–8*). Some reports from studies using the same electrodes are also available on mixed aqueous aprotic solvents such as H_2O–DMSO (*9*), water–acetonitrile (*10*), and water–acetone (*11*). However, only a few data are available on these electrodes in isodielectric media such as ethylene glycol–acetonitrile (*12*), methanol–acetonitrile (*13*), methanol–propylene glycol (*14*a,b), ethylene glycol–diethylene glycol (*15*), and ethylene glycol–dimethylformamide (*16*). The use of such isodielectric solvent mixtures provides the possibility of eliminating electrostatic effects so that the chemical effects of the solvent mixtures on ion–solvent interactions can be examined. Hence, in the present study, which is in continuation of our earlier work (*17*,*18*) in mixed solvents containing dimethylformamide (DMF), we report the standard potentials of Ag–AgCl and Ag–AgBr electrodes in the nearly isodielectric mixtures of glycerol–DMF at three different temperatures. The various thermodynamic parameters associated with the transfer of HCl and HBr have been evaluated, and the significance of the various thermodynamic parameters is discussed.

Table I. Physical Constants and Other Data of Glycerol–Dimethylformamide Mixtures at Various Temperatures[a]

wt % DMF		25 °C	30 °C	35 °C	M_{xy}
10	D	42	40.6	39.3	89.68
	A'	1.3017	1.3358	1.3686	
	$B' \times 10^{-8}$	0.4494	0.4533	0.4570	
	d_0	1.2205	1.2175	1.2131	
20	D	41.7	40.2	39.0	87.47
	A'	1.3157	1.3558	1.3845	
	$B' \times 10^{-8}$	0.4510	0.4556	0.4587	
	d_0	1.1853	1.1824	1.1789	
40	D	41.2	40.0	38.7	
	A'	1.3397	1.3660	1.4006	83.37
	$B' \times 10^{-8}$	0.4537	0.4567	0.4605	
	d_0	1.1176	1.1149	1.1101	
60	D	40.3	39.3	38.4	79.64
	A'	1.3849	1.4026	1.4170	
	$B' \times 10^{-8}$	0.4588	0.4607	0.4623	
	d_0	1.0556	1.0524	1.0479	

[a] D = dielectric constant, A' and B' = Debye–Hückel constants, M_{xy} = mean molecular weight.

Experimental Section

The emf measurements have been made in the composition range 10–60 wt % DMF (for HCl) and 10–40 wt % DMF (for HBr) at 25, 30, and 35 °C with the cell

$$\text{Pt},H_2\ (\text{g, 1 atm})|\text{HX}\ (m),\ \text{DMF (x)–Gly (y)}|\text{AgX–Ag} \qquad (1)$$

$$X = Cl^- \text{ or } Br^-$$

Glycerol (Merck) was purified by heating it to 100 °C to remove traces of moisture, and then it was distilled under reduced pressure. The purification of other solvents and preparation of experimental solutions have been described earlier (*17*). In the case of HBr, the gas was generated by the dropwise addition of liquid bromine to tetralin and this gas was passed through traps containing tetralin and a solvent mixture and then finally absorbed in the solvent mixture to get the required strength of HBr. The Ag–AgX electrodes were of thermal electrolytic type (*19*) and had bias potentials less than 0.05 mV 3 days after the electrolysis. The hydrogen electrodes were prepared in accordance with the method of Hills and Ives (*20*). Other experimental details such as temperature control, the determination of dielectric constants, and densities of solvent mixtures at various temperatures have been described earlier (*17*). The

0021-9568/90/1735-0008$02.50/0