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Density, Viscosity and Refraction Index of Aqueous Solutions of 7-Hydroxycoumarin and Ethanol or 1-Propanol at Temperatures from 293.15 to 313.15 K

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Abstract 7-Hydroxycoumarin exhibits antioxidative, lipoxygenase inhibitive and anti-tumourigenic effects. Density and viscosity measurements have been carried out for the solutions of 7-hydroxycoumarin in mixture solvents of water and ethanol or 1-propanol at $T = (293.15, 298.15, 303.15, 308.15$ and $313.15)$ K. The measured data have been used to evaluate apparent molar volumes (V_ϕ), limiting apparent molar volumes (V_ϕ^0), viscosity B-coefficients of the Jones–Dole equation and variation of B with temperature (dB/dT). The values of V_ϕ^0 and B-coefficients are positive and pass through their corresponding maxima at about 18 mol·kg^{-1} ethanol molality and 20 mol·kg^{-1} 1-propanol molality, respectively. Besides, the values of V_ϕ^0 and B-coefficients decrease with increasing temperature. Molar refractive indices (R_D) of the ternary solutions at the temperature of 298.15 K have also been determined from measured refractive indices (n_D). There is an obvious increase of R_D with increasing molality of the solvent. These parameters have been interpreted in terms of solute–solvent interactions and structure making/breaking ability of components in the aqueous solution. The temperature and concentration dependences of the weak interactions in the solution systems have also been discussed.

Keywords 7-Hydroxycoumarin · Density · Viscosity · Refractive index · Ethanol · 1-Propanol

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1 Introduction

Coumarin (1,2–benzopyrone) is a widely distributed natural product with low human toxicity [1]. It can slow the development of both renal and prostate carcinoma and prevent the recurrence of melanoma [2, 3]. The major biotransformation product of coumarin in the human body is 7-hydroxycoumarin (7-HC) [4]. Several reports have shown that 7-HC has antioxidative, lipoxygenase inhibitive and anti-tumourigenic effects [5–7]. However, the molecular action mechanism of 7-HC is unknown.

A systematic knowledge of the solution behavior of drugs can be of great significance in understanding their physiological action, which can be achieved with the help of thermodynamic and transport property measurements [8]. Testa et al. [9] examined the viscosity of binary mixtures of water and aprotic or protic polar solvents and compared the results with the viscosity of binary mixtures of aprotic polar solvents. This study indicated that binary mixtures of miscible solvents may provide a valuable means for investigating and assessing intermolecular interaction, and they are used as model systems in a pharmaceutical perspective. Aqueous solutions of alcohols have found wide application in pharmaceutical and cosmetic industries. When introduced into a living organism as vehicles for pharmaceuticals or cosmetics, they affect the components of cellular fluids. Thus the behavior of 7-HC in aqueous alcohol solutions may be important from pharmacological and industrial viewpoints [10].

Volumetric properties of solutions, such as apparent molar volumes and limiting partial molar volumes, are very useful to explain the intermolecular interaction occurring in these solutions [11, 12]. Viscometric methods have been successfully used to access the parameters of various biological molecules [13, 14]. The simultaneous investigation of volume and viscosity effects on mixing is a powerful tool for the interpretation of intermolecular interactions present in these mixtures. They also throw light on solute–solvent interactions, which correlate with the structure making/breaking properties of the solutes and solvents. In addition, the refractive index of drugs in aqueous solutions is another parameter to determine the molecular interactions occurred in aqueous systems.

Banipal et al. [15] have reported the volumetric and viscometric properties of some sulpha drugs in aqueous sodium chloride solutions at $T = (288.15$ to $318.15)$ K and interpreted their results in terms of interactions between solute and solvent. Iqbal et al. [16] have measured the viscosities and densities of salicyl amide, salicylic acid, and acetyl salicylic acid in alcohols from 293.15 to 313.15 K and shown that the drug molecules are regarded as structure-makers owing to the breakup of their hydration shell due to thermal motion. However, to the best of our knowledge, no work has been reported on the physicochemical effects of alcohols on 7-HC. So, the aim of the present work is to elucidate the hydration characteristic of 7-HC in aqueous alcohol solutions. In the work to be presented here, densities, viscosities of 7-HC + ethanol/1-propanol + water solutions have been measured at $T = (293.15, 298.15, 303.15, 308.15$ and $313.15)$ K. These values are used to compute apparent molar volumes (V_ϕ), limiting partial molar volumes (V_ϕ^0) and viscosity B-coefficients of 7-HC. In addition, molar refractive indices (R_D) of the ternary mixtures at 298.15 K have been acquired from the experimental values of refractive indices (n_D). All of these parameters are discussed in terms of solute–solvent interactions occurring in the (7-HC + ethanol/1-propanol + water) systems. These results may be helpful for understanding the functional properties of 7-HC in the human body.

2 Experimental

2.1 Materials

7-HC was purchased from J & K Chemical, Ltd. (Beijing, China) and the stated mass fraction purity is better than 0.98. Ethanol and 1-propanol were available from Tianjin Kermel Chemical Reagent Company (Tianjin, China) and their purities are above 0.997 and 0.995 mass fractions, respectively. All the reagents were used without further purification. Doubly distilled water was used.

2.2 Solution Preparation

Stock solutions of aqueous ethanol or 1-propanol were prepared using double distilled water at 298.15 K and were used as solvents for the preparation of the 7-HC solutions. Solutions of aqueous alcohol and aqueous 7-HC solutions in the concentration range of (14.00–22.00) mol·kg^{-1} and (0–0.0300) mol·kg^{-1} were prepared by mass on a Mettler Toledo AG 135 analytical balance with a precision of ±0.00001 g. All the solutions were stored in special air tight bottles to avoid evaporation. All the solutions were used within 12 h after preparation to minimize decomposition.

2.3 Density Measurements

The densities of solutions were measured by a quartz vibrating-tube densimeter (Anton Paar DMA 5000) thermostated to ±0.001 K. The precision of the densimeter was $\pm 5 \times 10^{-6}$ g·cm^{-3}. The densimeter was calibrated with double-distilled deionized water and dry air at $T = 293.15$ K [17, 18]. The estimated uncertainties of measured densities were found to be within 0.0005 g·cm^{-3}. The final results are the average of triplicate measurements for each sample.

2.4 Viscosity Measurements

Viscosity measurements were carried out with a suspended level Ubbelohde viscometer. The viscometer was calibrated with double-distilled deionized water. The viscosity values of water at different temperatures were taken from Perry's Chemical Engineers' Handbook [19]. An electronic digital stopwatch with an accuracy of ±0.01 s was used for flow-time measurements. As the flow times were greater than 100 s, the kinetic energy corrections are not necessary [20]. The Ubbelhode viscometer, filled with test solutions, was allowed to stand for about 30 min in an electronically controlled thermostatic water bath so as to maintain the temperatures of the solutions to an accuracy of ±0.01 K. An average of four or five readings with reproducibilities within 0.1 s was used as final flow time. The dynamic viscosity of solutions was calculated using

$$\eta/\eta_0 = (\rho t)/(\rho_0 t_0) \quad (1)$$

where ρ, ρ_0, t, t_0, and η, η_0 are density, flow time, and viscosity of the drug solutions (7-HC + ethanol/1-propanol + water) and the solvents (ethanol/1-propanol + water), respectively. The calculated viscosities have an uncertainty within ±0.003 mPa·s.

2.5 Refractive Index Measurement

Refractive indices were measured with a model-2 W refractometer (Shanghai, China). The calibration was done with pure water whose measured refraction index at 298.15 K is 1.3326. This value agreed well with that in the literature [21]. The temperature of the test solution during the measurements was maintained within an uncertainty of ±0.01 K in an electronically controlled thermostatic water bath. The uncertainty in the refractive index was found to be within ±0.0003. All the data shown in Table 5 represent the average of three iterations.

3 Results and Discussion

3.1 Volumetric Properties

The experimental density values of 7-HC + ethanol/1-propanol + water mixtures at different temperatures are listed in Table 1. The apparent molar volumes V_ϕ of 7-HC in the ternary systems were calculated by the following equation [22, 23]:

$$V_\varphi = \frac{M}{\rho} - 1000\frac{(\rho - \rho_0)}{m\rho\rho_0} \tag{2}$$

where M and m are the molar mass and molality of 7-HC, respectively. The values of V_φ are also listed in Table 1.

A linear dependence of V_φ on m was observed over the concentration range studied. Linear regression analysis of V_φ was carried out to find the partial molar volume at infinite dilution (V_ϕ^0) as follows [24, 25]:

$$V_\phi = V_\phi^0 + S_V m \tag{3}$$

where S_v is the experimental slope. The experimental S_v values for the investigated ternary systems are found to be positive but are smaller than V_ϕ^0. This shows the existence of weak interactions between solute molecules, in comparison to stronger solute–solvent interactions. Therefore, the values of S_V have not been reported in the tables. The data of limiting partial molar volumes of 7-HC in infinite dilution solutions were calculated and are summarized in Table 2.

It can be found from a perusal of Table 2 that the values of the limiting apparent molar volume, V_ϕ^0, are positive in the mixtures of water and ethanol/1-propanol, which can provide information regarding solute–solvent interactions. Relative to water, the types of interactions occurring between 7-HC and alcohol molecules can be classified as follows:

1) Hydrophilic–hydrophilic interactions between the –OH groups in 7-HC and the alcohol molecules mediated through intermolecular hydrogen bonding.
2) Hydrophilic–hydrophobic interactions between the –OH group and the alkyl group in 7-HC and the alcohol molecules, respectively.
3) Hydrophobic–hydrophobic interactions between the benzofuran ring of 7-HC and the alkyl groups of alcohol molecules.

The interaction of type (i) leads to a positive contribution to V_ϕ^0 while those of types (ii) and (iii) lead to opposite contributions as a result of cosphere overlap. The positive values

Table 1 Values of densities (ρ) and apparent molar volumes (V_ϕ) of 7-HC in aqueous ethanol and 1-propanol solutions at T = (293.15, 298.15, 303.15, 308.15, and 313.15) K. ($m_{7\text{-HC}}$– molality of 7-HC based on kilogram of the mixed solvent, $m_{\text{ethanol}}/m_{1\text{-propanol}}$– molality of ethanol/1-propanol based on kilogram of water)

$\frac{m_{7-HC}}{mol \cdot kg^{-1}}$	$\frac{\rho}{g \cdot cm^{-3}}$ 293.15 K	$\frac{V_\phi}{cm^3 \cdot mol^{-1}}$	$\frac{\rho}{g \cdot cm^{-3}}$ 298.15 K	$\frac{V_\phi}{cm^3 \cdot mol^{-1}}$	$\frac{\rho}{g \cdot cm^{-3}}$ 303.15 K	$\frac{V_\phi}{cm^3 \cdot mol^{-1}}$	$\frac{\rho}{g \cdot cm^{-3}}$ 308.15 K	$\frac{V_\phi}{cm^3 \cdot mol^{-1}}$	$\frac{\rho}{g \cdot cm^{-3}}$ 313.15 K	$\frac{V_\phi}{cm^3 \cdot mol^{-1}}$
$m_{ethanol}$ = 14.00 mol·kg^{-1}										
0.0000	0.936706		0.933024		0.929265		0.925437		0.921529	
0.0100	0.937358	98.78 ± 0.32	0.933692	96.98 ± 0.32	0.929959	94.10 ± 0.33	0.926154	91.41 ± 0.33	0.922278	87.68 ± 0.33
0.0150	0.937680	99.04 ± 0.21	0.934022	97.30 ± 0.22	0.930302	94.41 ± 0.22	0.926508	91.78 ± 0.22	0.922648	88.05 ± 0.22
0.0200	0.937997	99.32 ± 0.16	0.934347	97.58 ± 0.16	0.930639	94.71 ± 0.16	0.926857	92.08 ± 0.17	0.923011	88.46 ± 0.16
0.0247	0.938295	99.55 ± 0.13	0.934652	97.83 ± 0.13	0.930955	95.01 ± 0.13	0.927183	92.42 ± 0.13	0.923353	88.74 ± 0.13
0.0300	0.938628	99.83 ± 0.11	0.934992	98.17 ± 0.11	0.931308	95.36 ± 0.11	0.927548	92.77 ± 0.11	0.923734	89.13 ± 0.11
$m_{ethanol}$ = 16.00 mol·kg^{-1}										
0.0000	0.930583		0.926799		0.922942		0.919015		0.915018	
0.0100	0.931205	102.34 ± 0.33	0.927436	100.68 ± 0.33	0.923605	97.83 ± 0.33	0.919701	95.13 ± 0.33	0.915740	90.89 ± 0.34
0.0150	0.931512	102.61 ± 0.22	0.927750	101.02 ± 0.22	0.923930	98.24 ± 0.22	0.920038	95.54 ± 0.22	0.916093	91.48 ± 0.23
0.0200	0.931815	102.93 ± 0.16	0.928060	101.40 ± 0.16	0.924252	98.60 ± 0.17	0.920371	95.97 ± 0.17	0.916443	91.91 ± 0.17
0.0250	0.932116	103.23 ± 0.13	0.928368	101.68 ± 0.13	0.924571	98.98 ± 0.13	0.920703	96.28 ± 0.14	0.916790	92.33 ± 0.14
0.0300	0.932415	103.47 ± 0.11	0.928671	102.05 ± 0.11	0.924887	99.31 ± 0.11	0.921029	96.67 ± 0.11	0.917132	92.76 ± 0.11
$m_{ethanol}$ = 18.00 mol·kg^{-1}										
0.0000	0.924182		0.920298		0.916351		0.912337		0.908255	
0.0100	0.924773	106.31 ± 0.33	0.920905	104.57 ± 0.33	0.916982	101.80 ± 0.34	0.912988	99.52 ± 0.34	0.908924	97.49 ± 0.34
0.0150	0.925062	106.63 ± 0.22	0.921200	105.05 ± 0.22	0.917291	102.22 ± 0.22	0.913307	99.89 ± 0.23	0.909251	97.89 ± 0.23
0.0200	0.925349	106.99 ± 0.17	0.921494	105.44 ± 0.17	0.917596	102.67 ± 0.17	0.913623	100.33 ± 0.17	0.909575	98.37 ± 0.17
0.0250	0.925634	107.35 ± 0.13	0.921786	105.79 ± 0.14	0.917899	103.09 ± 0.14	0.913935	100.81 ± 0.14	0.909896	98.83 ± 0.14
0.0300	0.925913	107.68 ± 0.11	0.922072	106.15 ± 0.11	0.918197	103.45 ± 0.11	0.914242	101.21 ± 0.11	0.910210	99.30 ± 0.11

Table 1 continued

$\frac{m_{7\text{-HC}}}{\text{mol·kg}^{-1}}$	$\frac{\rho}{\text{g·cm}^{-3}}$ 293.15 K	$\frac{V_\phi}{\text{cm}^3\text{·mol}^{-1}}$	$\frac{\rho}{\text{g·cm}^{-3}}$ 298.15 K	$\frac{V_\phi}{\text{cm}^3\text{·mol}^{-1}}$	$\frac{\rho}{\text{g·cm}^{-3}}$ 303.15 K	$\frac{V_\phi}{\text{cm}^3\text{·mol}^{-1}}$	$\frac{\rho}{\text{g·cm}^{-3}}$ 308.15 K	$\frac{V_\phi}{\text{cm}^3\text{·mol}^{-1}}$	$\frac{\rho}{\text{g·cm}^{-3}}$ 313.15 K	$\frac{V_\phi}{\text{cm}^3\text{·mol}^{-1}}$
$m_{\text{ethanol}} = 20.00\ \text{mol·kg}^{-1}$										
0.0000	0.918792		0.914849		0.910842		0.906770		0.902632	
0.0100	0.919421	101.90 ± 0.34	0.915496	99.89 ± 0.34	0.911509	97.61 ± 0.34	0.907453	95.68 ± 0.34	0.903347	91.81 ± 0.35
0.0150	0.919731	102.14 ± 0.22	0.915814	100.22 ± 0.23	0.911836	97.95 ± 0.23	0.907789	96.00 ± 0.23	0.903698	92.21 ± 0.23
0.0200	0.920039	102.46 ± 0.17	0.916130	100.55 ± 0.17	0.912162	98.30 ± 0.17	0.908122	96.43 ± 0.17	0.904049	92.54 ± 0.17
0.0249	0.920337	102.79 ± 0.13	0.916437	100.85 ± 0.14	0.912479	98.61 ± 0.14	0.908444	96.86 ± 0.14	0.904385	93.04 ± 0.14
0.0300	0.920645	103.09 ± 0.11	0.916752	101.22 ± 0.11	0.912803	99.02 ± 0.11	0.908778	97.19 ± 0.11	0.904733	93.45 ± 0.12
$m_{\text{ethanol}} = 22.00\ \text{mol·kg}^{-1}$										
0.0000	0.913462		0.909466		0.905406		0.901281		0.897097	
0.0100	0.914108	100.01 ± 0.34	0.910125	98.54 ± 0.34	0.906091	95.45 ± 0.35	0.901989	92.73 ± 0.35	0.897835	89.03 ± 0.35
0.0150	0.914427	100.24 ± 0.23	0.910451	98.77 ± 0.23	0.906428	95.80 ± 0.23	0.902338	93.02 ± 0.23	0.898198	89.40 ± 0.23
0.0200	0.914744	100.54 ± 0.17	0.910773	99.13 ± 0.17	0.906763	96.16 ± 0.17	0.902684	93.42 ± 0.17	0.898558	89.82 ± 0.18
0.0250	0.915060	100.78 ± 0.14	0.911095	99.39 ± 0.14	0.907096	96.50 ± 0.14	0.903027	93.81 ± 0.14	0.898917	90.19 ± 0.14
0.0300	0.915370	101.06 ± 0.11	0.911410	99.71 ± 0.11	0.907424	96.79 ± 0.12	0.903365	94.15 ± 0.12	0.899267	90.63 ± 0.12
$m_{\text{1-propanol}} = 14.00\ \text{mol·kg}^{-1}$										
0.0000	0.918103		0.914486		0.910811		0.907075		0.903277	
0.0100	0.918682	107.93 ± 0.34	0.915084	105.76 ± 0.34	0.911423	104.21 ± 0.34	0.907711	101.43 ± 0.34	0.903934	98.95 ± 0.35
0.0149	0.918961	108.21 ± 0.22	0.915373	106.04 ± 0.23	0.911717	104.60 ± 0.23	0.908016	101.87 ± 0.23	0.904251	99.26 ± 0.23
0.0200	0.919249	108.52 ± 0.17	0.915672	106.32 ± 0.17	0.912022	104.92 ± 0.17	0.908333	102.20 ± 0.17	0.904577	99.76 ± 0.17
0.0250	0.919529	108.75 ± 0.14	0.915958	106.71 ± 0.14	0.912316	105.26 ± 0.14	0.908639	102.52 ± 0.14	0.904891	100.18 ± 0.14
0.0300	0.919806	109.05 ± 0.11	0.916245	106.98 ± 0.11	0.912607	105.64 ± 0.11	0.908941	102.94 ± 0.11	0.905205	100.52 ± 0.12
$m_{\text{1-propanol}} = 16.00\ \text{mol·kg}^{-1}$										
0.0000	0.911211		0.907532		0.903797		0.899995		0.896130	
0.0100	0.911770	110.60 ± 0.34	0.908109	108.59 ± 0.34	0.904379	108.08 ± 0.35	0.900591	106.50 ± 0.35	0.896749	103.78 ± 0.35
0.0150	0.912044	110.92 ± 0.23	0.908391	108.99 ± 0.23	0.904665	108.41 ± 0.23	0.900883	106.92 ± 0.23	0.897052	104.24 ± 0.23

Table 1 continued

$m_{7\text{-HC}}$ / mol·kg^{-1}	ρ / g·cm^{-3}	V_ϕ / cm^3·mol^{-1}	ρ / g·cm^{-3}	V_ϕ / cm^3·mol^{-1}	ρ / g·cm^{-3}	V_ϕ / cm^3·mol^{-1}	ρ / g·cm^{-3}	V_ϕ / cm^3·mol^{-1}	ρ / g·cm^{-3}	V_ϕ / cm^3·mol^{-1}
	293.15 K		298.15 K		303.15 K		308.15 K		313.15 K	
0.0200	0.912316	111.24 ± 0.17	0.908671	109.36 ± 0.17	0.904948	108.78 ± 0.17	0.901173	107.27 ± 0.17	0.897353	104.62 ± 0.18
0.0250	0.912585	111.60 ± 0.14	0.908948	109.75 ± 0.14	0.905228	109.18 ± 0.14	0.901458	107.76 ± 0.14	0.897649	105.12 ± 0.14
0.0300	0.912851	111.87 ± 0.11	0.909222	110.03 ± 0.11	0.905503	109.55 ± 0.12	0.901738	108.19 ± 0.12	0.897940	105.56 ± 0.12
$m_{1\text{-propanol}}$ = 18.00 mol·kg^{-1}										
0.0000	0.905417		0.901687		0.897899		0.894048		0.890133	
0.0100	0.905931	116.31 ± 0.35	0.902226	113.46 ± 0.35	0.898471	109.56 ± 0.35	0.894637	107.60 ± 0.35	0.890733	106.36 ± 0.36
0.0149	0.906183	116.69 ± 0.23	0.902489	113.91 ± 0.23	0.898751	109.97 ± 0.23	0.894924	108.14 ± 0.24	0.891025	106.94 ± 0.24
0.0200	0.906433	117.00 ± 0.17	0.902751	114.24 ± 0.17	0.899029	110.36 ± 0.18	0.895210	108.52 ± 0.18	0.891316	107.35 ± 0.18
0.0250	0.906677	117.42 ± 0.14	0.903008	114.65 ± 0.14	0.899301	110.84 ± 0.14	0.895492	108.93 ± 0.14	0.891600	107.90 ± 0.14
0.0300	0.906920	117.79 ± 0.12	0.903262	115.07 ± 0.12	0.899570	111.31 ± 0.12	0.895767	109.48 ± 0.12	0.891881	108.43 ± 0.12
$m_{1\text{-propanol}}$ = 20.00 mol·kg^{-1}										
0.0000	0.899512		0.895724		0.891885		0.887984		0.884020	
0.0100	0.900018	117.67 ± 0.35	0.896247	115.84 ± 0.35	0.892420	114.49 ± 0.36	0.888541	111.91 ± 0.36	0.884584	111.19 ± 0.36
0.0149	0.900266	118.00 ± 0.23	0.896501	116.33 ± 0.24	0.892682	114.87 ± 0.24	0.888812	112.50 ± 0.24	0.884859	111.70 ± 0.24
0.0200	0.900510	118.44 ± 0.17	0.896752	116.80 ± 0.18	0.892940	115.33 ± 0.18	0.889081	112.88 ± 0.18	0.885131	112.17 ± 0.18
0.0250	0.900749	118.91 ± 0.14	0.897000	117.20 ± 0.14	0.893193	115.82 ± 0.14	0.889345	113.34 ± 0.15	0.885399	112.62 ± 0.15
0.0300	0.900987	119.29 ± 0.12	0.897245	117.62 ± 0.12	0.893442	116.34 ± 0.12	0.889604	113.90 ± 0.12	0.885661	113.20 ± 0.12
$m_{1\text{-propanol}}$ = 22.00 mol·kg^{-1}										
0.0000	0.895376		0.891557		0.887682		0.883751		0.879756	
0.0100	0.895942	110.38 ± 0.35	0.892130	109.67 ± 0.36	0.888272	107.73 ± 0.36	0.884349	106.79 ± 0.36	0.880373	104.47 ± 0.37
0.0149	0.896221	110.68 ± 0.24	0.892411	110.09 ± 0.24	0.888560	108.23 ± 0.24	0.884643	107.18 ± 0.24	0.880677	104.82 ± 0.24
0.0200	0.896497	111.03 ± 0.18	0.892688	110.58 ± 0.18	0.888846	108.68 ± 0.18	0.884931	107.78 ± 0.18	0.880975	105.41 ± 0.18
0.0250	0.896769	111.35 ± 0.14	0.892961	110.98 ± 0.14	0.889126	109.09 ± 0.15	0.885217	108.17 ± 0.15	0.881268	105.91 ± 0.15
0.0300	0.897037	111.77 ± 0.12	0.893233	111.32 ± 0.12	0.889405	109.52 ± 0.12	0.885498	108.64 ± 0.12	0.881560	106.34 ± 0.12

Table 2 Limiting partial molar volumes (V_ϕ^0) of 7-HC in aqueous ethanol and 1-propanol solutions at $T = (293.15, 298.15, 303.15, 308.15, \text{and } 313.15)$ K (m_{solvent}– molality of ethanol or 1-propanol based on kilogram of water)

m_{solvent} (mol·kg^{-1})	V_ϕ^0 (cm^3·mol^{-1})				
	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
Ethanol					
14.00	98.26 ± 0.01	96.40 ± 0.02	93.47 ± 0.01	90.74 ± 0.02	86.97 ± 0.04
16.00	101.76 ± 0.03	100.01 ± 0.03	97.11 ± 0.03	94.39 ± 0.05	90.04 ± 0.08
18.00	105.61 ± 0.02	103.84 ± 0.06	100.98 ± 0.04	98.63 ± 0.04	96.55 ± 0.03
20.00	101.26 ± 0.04	99.22 ± 0.02	96.90 ± 0.03	94.88 ± 0.06	90.96 ± 0.06
22.00	99.47 ± 0.02	97.92 ± 0.04	94.79 ± 0.03	91.97 ± 0.04	88.22 ± 0.03
1-Propanol					
14.00	107.38 ± 0.03	105.12 ± 0.05	103.52 ± 0.03	100.73 ± 0.06	98.11 ± 0.07
16.00	109.96 ± 0.03	107.89 ± 0.05	107.32 ± 0.03	105.64 ± 0.05	102.89 ± 0.04
18.00	115.57 ± 0.04	112.69 ± 0.05	108.67 ± 0.05	106.72 ± 0.08	105.36 ± 0.06
20.00	116.81 ± 0.05	114.99 ± 0.05	113.51 ± 0.06	110.98 ± 0.09	110.21 ± 0.05
22.00	109.67 ± 0.05	108.86 ± 0.06	106.88 ± 0.04	105.84 ± 0.07	103.46 ± 0.08

of V_ϕ^0 suggest that the hydrophilic–hydrophilic interactions are dominant in the ternary solutions.

Figure 1 shows that the values of V_ϕ^0 pass through a maximum at about 18 mol·kg^{-1} ethanol molality in the range of the aqueous ethanol solutions investigated. The tendency of V_ϕ^0 versus the molality of 1-propanol is very close to that in the aqueous ethanol system, except that the molality of 1-propanol corresponding to the maximum value of V_ϕ^0 is about 20 mol·kg^{-1}. So the plot of V_ϕ^0 versus the molality of 1-propanol was omitted. The maximum value of V_ϕ^0 can be explained as follows. On one hand, ethanol molecules may be accommodated in the hydrophobic hydration sheath around 7-HC at lower concentrations [26]. The hydrogen bonding interactions between the –OH groups of alcohol molecules and water molecules in the hydrophobic hydration shell of 7-HC results in the weakness of hydrophobic interactions. Less water molecules are released into the bulk phase from the hydrophobic hydration sheath. This makes a positive contribution to V_ϕ^0. With the increase of the alcohol molality, the hydrogen bonding interactions are maximized, corresponding to the maximum value of V_ϕ^0. On the other hand, a further increase of alcohol contents enhances the hydrophilic–hydrophobic and hydrophobic–hydrophobic interactions, which are responsible for the decrease of V_ϕ^0. The maximum value of V_ϕ^0 at about 20 mol·kg^{-1} 1-propanol molality may be caused by the longer alkyl chain of 1-propanol. The stronger hydrophobicity of 1-propanol attenuates the hydrogen bonding interactions. Therefore, the maximum value of V_ϕ^0 occurs at a higher concentration of 1-propanol.

The values of V_ϕ^0 decrease with temperature for the aqueous ethanol and propanol systems. This is a characteristic property of aqueous solutions of hydrophobic solutes [27]. The hydrophobic hydration decreases at higher temperatures [28]; some water molecules are released from hydrophobic hydration shells which leads to a negative contribution to V_ϕ^0.

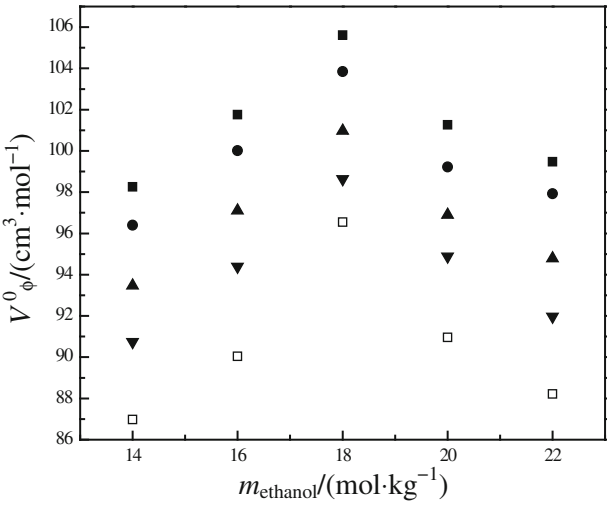

Fig. 1 Variation of the limiting partial molar volume of 7-HC (V^0_ϕ) versus the molality of ethanol in aqueous solutions at $T = 293.15$ K (*filled square*), 298.15 K (*filled circle*), 303.15 K (*filled triangle*), 308.15 K (*filled inverted triangle*), and 313.15 K (*square*)

From Table 2, it is evident that the limiting partial molar volumes of 7-HC in aqueous 1-propanol solutions are larger than those in aqueous ethanol solutions in the temperature range studied here. This is due to the longer hydrophobic chain of 1-propanol. The longer alkyl chain results in reinforced hydrogen bonding interactions between water molecules surrounding these apolar groups [29]. The cooperativity of hydrogen bonding reinforces the interaction between water molecules in hydration layers and hydroxyl groups of alcohol molecules. The final result is the weakness of hydrophobic interactions, which leads to the increase of V^0_ϕ.

3.2 Viscometric Properties

The interaction of solute–solvent can also be discussed with the change of a dynamic property such as viscosity. The viscosity data given in Table 3 are analyzed with the Jones–Dole equation [15]:

$$(\eta/\eta_0 - 1)/c^{1/2} = A + Bc^{1/2} \tag{4}$$

where c is the molar concentration of 7-HC (calculated from molality and density data) in the solution. The A-coefficient reflects solute–solute interactions, and B-coefficient depends upon solute–solvent interactions and the relative size of solute and solvent molecules [30]. In the case of non-electrolytes, $A = 0$, and the Jones-Dole equation is simplified to the form [27, 31]:

$$\eta_r = 1 + Bc \tag{5}$$

where the B-coefficients were obtained from the linear plots of η_r versus c and are given in Table 4. From Table 3, it can be seen that the viscosities of 7-HC–alcohol–water systems are higher than those of the corresponding alcohol–water systems (solvent). This might

Table 3 Values of viscosities (η) of 7-HC in aqueous ethanol and 1-propanol solutions at $T = (293.15, 298.15, 303.15, 308.15, \text{and } 313.15)$ K. ($m_{\text{7-HC}}$–molality of 7-HC based on kilogram of the mixed solvent, $m_{\text{ethanol}}/m_{\text{1-propanol}}$ – molality of ethanol/1-propanol based on kilogram of water)

$m_{\text{7-HC}}$ (mol·kg^{-1})	η(mPa·s)									
	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
$m_{\text{ethanol}} = 14.00$ (mol·kg^{-1})						$m_{\text{1-propanol}} = 14.00$ mol·kg^{-1}				
0.0000	2.895 ± 0.027	2.350 ± 0.022	1.970 ± 0.018	1.673 ± 0.016	1.440 ± 0.013	3.110 ± 0.029	2.599 ± 0.024	2.193 ± 0.020	1.880 ± 0.017	1.626 ± 0.015
0.0100	2.900 ± 0.027	2.353 ± 0.022	1.972 ± 0.018	1.674 ± 0.016	1.440 ± 0.013	3.119 ± 0.029	2.606 ± 0.024	2.199 ± 0.020	1.884 ± 0.018	1.629 ± 0.015
0.0150	2.902 ± 0.027	2.355 ± 0.022	1.973 ± 0.018	1.675 ± 0.016	1.441 ± 0.013	3.124 ± 0.029	2.609 ± 0.024	2.201 ± 0.020	1.886 ± 0.018	1.630 ± 0.015
0.0200	2.905 ± 0.027	2.357 ± 0.022	1.975 ± 0.018	1.676 ± 0.016	1.442 ± 0.013	3.128 ± 0.029	2.612 ± 0.024	2.204 ± 0.020	1.888 ± 0.018	1.632 ± 0.015
0.0250	2.908 ± 0.027	2.359 ± 0.022	1.976 ± 0.018	1.677 ± 0.016	1.443 ± 0.013	3.132 ± 0.029	2.615 ± 0.024	2.206 ± 0.020	1.890 ± 0.018	1.633 ± 0.015
0.0300	2.910 ± 0.027	2.361 ± 0.022	1.978 ± 0.018	1.678 ± 0.016	1.444 ± 0.013	3.136 ± 0.029	2.618 ± 0.024	2.209 ± 0.020	1.891 ± 0.018	1.635 ± 0.015
$m_{\text{ethanol}} = 16.00$ mol·kg^{-1}						$m_{\text{1-propanol}} = 16.00$ mol·kg^{-1}				
0.0000	2.900 ± 0.027	2.363 ± 0.022	1.988 ± 0.018	1.690 ± 0.016	1.456 ± 0.014	3.151 ± 0.029	2.637 ± 0.025	2.230 ± 0.021	1.906 ± 0.018	1.648 ± 0.015
0.0100	2.908 ± 0.027	2.369 ± 0.022	1.992 ± 0.019	1.693 ± 0.016	1.459 ± 0.014	3.161 ± 0.029	2.645 ± 0.025	2.236 ± 0.021	1.910 ± 0.018	1.652 ± 0.015
0.0150	2.912 ± 0.027	2.372 ± 0.022	1.994 ± 0.019	1.695 ± 0.016	1.460 ± 0.014	3.166 ± 0.029	2.648 ± 0.025	2.239 ± 0.021	1.913 ± 0.018	1.653 ± 0.015
0.0200	2.915 ± 0.027	2.375 ± 0.022	1.997 ± 0.019	1.696 ± 0.016	1.461 ± 0.014	3.170 ± 0.029	2.652 ± 0.025	2.242 ± 0.021	1.915 ± 0.018	1.655 ± 0.015
0.0250	2.919 ± 0.027	2.378 ± 0.022	1.999 ± 0.019	1.698 ± 0.016	1.462 ± 0.014	3.175 ± 0.030	2.655 ± 0.025	2.245 ± 0.021	1.917 ± 0.018	1.657 ± 0.015
0.0300	2.922 ± 0.027	2.381 ± 0.022	2.001 ± 0.019	1.700 ± 0.016	1.464 ± 0.014	3.180 ± 0.030	2.659 ± 0.025	2.248 ± 0.021	1.919 ± 0.018	1.658 ± 0.015
$m_{\text{ethanol}} = 18.00$ mol·kg^{-1}						$m_{\text{1-propanol}} = 18.00$ mol·kg^{-1}				
0.0000	2.889 ± 0.027	2.365 ± 0.022	1.990 ± 0.019	1.695 ± 0.016	1.462 ± 0.014	3.176 ± 0.030	2.663 ± 0.025	2.255 ± 0.021	1.930 ± 0.018	1.670 ± 0.016
0.0100	2.900 ± 0.027	2.373 ± 0.022	1.997 ± 0.019	1.700 ± 0.016	1.466 ± 0.014	3.190 ± 0.030	2.674 ± 0.025	2.263 ± 0.021	1.936 ± 0.018	1.675 ± 0.016
0.0150	2.905 ± 0.027	2.377 ± 0.022	2.000 ± 0.019	1.702 ± 0.016	1.468 ± 0.014	3.196 ± 0.030	2.678 ± 0.025	2.266 ± 0.021	1.939 ± 0.018	1.677 ± 0.016
0.0200	2.910 ± 0.027	2.380 ± 0.022	2.002 ± 0.019	1.704 ± 0.016	1.469 ± 0.014	3.202 ± 0.030	2.682 ± 0.025	2.269 ± 0.021	1.941 ± 0.018	1.679 ± 0.016
0.0250	2.914 ± 0.027	2.384 ± 0.022	2.005 ± 0.019	1.706 ± 0.016	1.471 ± 0.014	3.207 ± 0.030	2.686 ± 0.025	2.272 ± 0.021	1.944 ± 0.018	1.681 ± 0.016
0.0300	2.919 ± 0.027	2.387 ± 0.022	2.008 ± 0.019	1.709 ± 0.016	1.473 ± 0.014	3.212 ± 0.030	2.690 ± 0.025	2.276 ± 0.021	1.946 ± 0.018	1.683 ± 0.016

Table 3 continued

$m_{7\text{-HC}}$ (mol·kg^{-1})	η(mPa·s)									
	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
$m_{\text{ethanol}} = 20.00$ mol·kg^{-1}						$m_{\text{1-propanol}} = 20.00$ mol·kg^{-1}				
0.0000	2.878 ± 0.027	2.371 ± 0.022	1.999 ± 0.019	1.704 ± 0.016	1.475 ± 0.014	3.178 ± 0.030	2.671 ± 0.025	2.263 ± 0.021	1.938 ± 0.018	1.679 ± 0.016
0.0100	2.889 ± 0.027	2.379 ± 0.022	2.005 ± 0.019	1.708 ± 0.016	1.478 ± 0.014	3.192 ± 0.030	2.682 ± 0.025	2.272 ± 0.021	1.945 ± 0.018	1.684 ± 0.016
0.0150	2.894 ± 0.027	2.382 ± 0.022	2.008 ± 0.019	1.710 ± 0.016	1.480 ± 0.014	3.198 ± 0.030	2.686 ± 0.025	2.275 ± 0.021	1.947 ± 0.018	1.687 ± 0.016
0.0200	2.898 ± 0.027	2.385 ± 0.02	2.010 ± 0.019	1.712 ± 0.016	1.481 ± 0.014	3.204 ± 0.030	2.691 ± 0.025	2.278 ± 0.021	1.950 ± 0.018	1.689 ± 0.016
0.0250	2.902 ± 0.027	2.388 ± 0.022	2.013 ± 0.019	1.714 ± 0.016	1.483 ± 0.014	3.210 ± 0.030	2.695 ± 0.025	2.282 ± 0.021	1.953 ± 0.018	1.691 ± 0.016
0.0300	2.905 ± 0.027	2.391 ± 0.022	2.015 ± 0.019	1.716 ± 0.016	1.484 ± 0.014	3.215 ± 0.030	2.700 ± 0.025	2.286 ± 0.021	1.956 ± 0.018	1.693 ± 0.016
$m_{\text{ethanol}} = 22.00$ mol·kg^{-1}						$m_{\text{1-propanol}} = 22.00$ mol·kg^{-1}				
0.0000	2.862 ± 0.027	2.352 ± 0.022	1.989 ± 0.019	1.700 ± 0.016	1.469 ± 0.014	3.191 ± 0.030	2.685 ± 0.025	2.277 ± 0.021	1.951 ± 0.018	1.690 ± 0.016
0.0100	2.871 ± 0.027	2.358 ± 0.022	1.993 ± 0.019	1.703 ± 0.016	1.471 ± 0.014	3.200 ± 0.030	2.692 ± 0.025	2.282 ± 0.021	1.954 ± 0.018	1.692 ± 0.016
0.0150	2.874 ± 0.027	2.361 ± 0.022	1.995 ± 0.019	1.704 ± 0.016	1.472 ± 0.014	3.205 ± 0.030	2.696 ± 0.025	2.284 ± 0.021	1.956 ± 0.018	1.694 ± 0.016
0.0200	2.878 ± 0.027	2.363 ± 0.022	1.997 ± 0.019	1.706 ± 0.016	1.473 ± 0.014	3.210 ± 0.030	2.699 ± 0.025	2.287 ± 0.021	1.958 ± 0.018	1.695 ± 0.016
0.0250	2.881 ± 0.027	2.366 ± 0.022	1.999 ± 0.019	1.707 ± 0.016	1.474 ± 0.014	3.214 ± 0.030	2.702 ± 0.025	2.290 ± 0.021	1.960 ± 0.018	1.697 ± 0.016
0.0300	2.885 ± 0.027	2.368 ± 0.022	2.001 ± 0.019	1.708 ± 0.016	1.475 ± 0.014	3.218 ± 0.030	2.705 ± 0.025	2.292 ± 0.021	1.962 ± 0.018	1.698 ± 0.016

Table 4 Viscosity *B*-coefficient (*B*) of 7-HC in aqueous ethanol and 1-propanol solutions at $T = (293.15, 298.15, 303.15, 308.15, \text{and } 313.15)$ K (m_{solvent}– molality of ethanol or 1-propanol based on kilogram of water)

m_{solvent} (mol·kg^{-1})	B (dm^3·mol^{-1})				
	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
Ethanol					
14.00	0.197 ± 0.002	0.182 ± 0.003	0.165 ± 0.003	0.142 ± 0.003	0.119 ± 0.004
16.00	0.270 ± 0.004	0.253 ± 0.002	0.231 ± 0.005	0.211 ± 0.004	0.190 ± 0.001
18.00	0.355 ± 0.005	0.323 ± 0.001	0.297 ± 0.004	0.271 ± 0.002	0.250 ± 0.004
20.00	0.312 ± 0.008	0.281 ± 0.005	0.262 ± 0.005	0.234 ± 0.002	0.210 ± 0.005
22.00	0.262 ± 0.003	0.237 ± 0.004	0.207 ± 0.003	0.177 ± 0.003	0.155 ± 0.004
1-Propanol					
14.00	0.292 ± 0.003	0.264 ± 0.003	0.247 ± 0.004	0.223 ± 0.004	0.195 ± 0.003
16.00	0.320 ± 0.002	0.296 ± 0.002	0.281 ± 0.005	0.263 ± 0.003	0.229 ± 0.002
18.00	0.385 ± 0.007	0.346 ± 0.004	0.315 ± 0.005	0.293 ± 0.003	0.271 ± 0.003
20.00	0.399 ± 0.003	0.372 ± 0.004	0.350 ± 0.007	0.320 ± 0.006	0.288 ± 0.002
22.00	0.306 ± 0.005	0.279 ± 0.003	0.257 ± 0.004	0.234 ± 0.003	0.205 ± 0.005

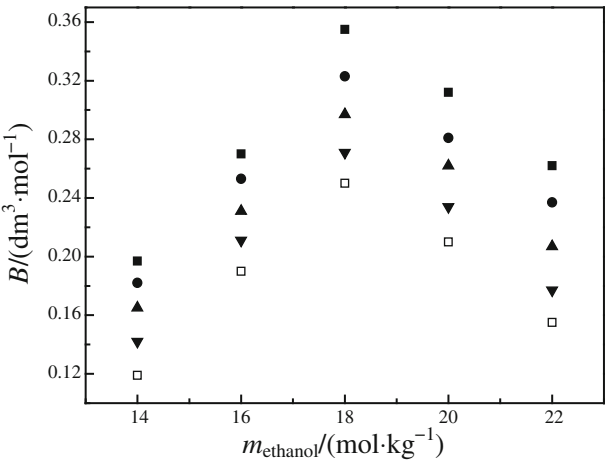

Fig. 2 Variation of viscosity *B*-coefficient of 7-HC versus the molality of ethanol in aqueous solution at $T = 293.15$ K (*filled square*), 298.15 K (*filled circle*), 303.15 K (*filled triangle*), 308.15 K (*filled inverted triangle*), 313.15 K (*square*)

indicate an increase in the net structure of the solvent; in this case solute–solvent bonds can be formed [32].

Second, the viscosity *B*-coefficients for 7-HC in the mixture solvents of water and alcohol are all positive and pass through a maximum at about 18 mol·kg^{-1} ethanol molality and 20 mol·kg^{-1} propanol molality, respectively. The *B*-coefficients of 7-HC in the mixed solvents of water and 1-propanol are more positive than those in aqueous ethanol solutions. A representative plot of *B*-coefficient versus the molality of ethanol is shown in Fig. 2. The positive value of the *B*-coefficient suggests hydrogen bonding of the solvent

Table 5 Refractive indices (n_D) and molar refraction (R_D) of 7-HC in aqueous ethanol and 1-propanol solutions at $T = 298.15$ K ($m_{7\text{-HC}}$ – molality of 7-HC based on kilogram of mixed solvent, $m_{ethanol}$/$m_{1\text{-propanol}}$ – molality of ethanol/1-propanol based on kilogram of water)

$m_{7\text{-HC}}$ (mol·kg^{-1})	n_D	$\frac{R_D}{cm^3 \cdot mol^{-1}}$	$m_{7\text{-HC}}$ (mol·kg^{-1})	n_D	$\frac{R_D}{cm^3 \cdot mol^{-1}}$
$m_{ethanol} = 14.00$ mol·kg^{-1}			$m_{1\text{-propanol}} = 14.00$ mol·kg^{-1}		
0.0000	1.3550	5.5267 ± 0.0041	0.0000	1.3640	6.4556 ± 0.0044
0.0100	1.3553	5.5346 ± 0.0041	0.0100	1.3642	6.4633 ± 0.0044
0.0150	1.3554	5.5379 ± 0.0041	0.0149	1.3644	6.4688 ± 0.0044
0.0200	1.3555	5.5412 ± 0.0041	0.0200	1.3645	6.4727 ± 0.0044
0.0247	1.3557	5.5460 ± 0.0041	0.0250	1.3646	6.4766 ± 0.0044
0.0300	1.3558	5.5492 ± 0.0041	0.0300	1.3647	6.4806 ± 0.0044
$m_{ethanol} = 16.00$ mol·kg^{-1}			$m_{1\text{-propanol}} = 16.00$ mol·kg^{-1}		
0.0000	1.3564	5.7314 ± 0.0042	0.0000	1.3654	6.7592 ± 0.0045
0.0100	1.3568	5.7412 ± 0.0042	0.0100	1.3659	6.7723 ± 0.0045
0.0150	1.3570	5.7461 ± 0.0042	0.0150	1.3662	6.7797 ± 0.0045
0.0200	1.3572	5.7510 ± 0.0042	0.0200	1.3665	6.7871 ± 0.0045
0.0250	1.3574	5.7559 ± 0.0042	0.0250	1.3667	6.7929 ± 0.0045
0.0300	1.3575	5.7595 ± 0.0041	0.0300	1.3669	6.7988 ± 0.0045
$m_{ethanol} = 18.00$ mol·kg^{-1}			$m_{1\text{-propanol}} = 18.00$ mol·kg^{-1}		
0.0000	1.3575	5.9292 ± 0.0042	0.0000	1.3670	7.0510 ± 0.0045
0.0100	1.3578	5.9379 ± 0.0042	0.0100	1.3673	7.0614 ± 0.0045
0.0150	1.3580	5.9430 ± 0.0042	0.0149	1.3675	7.0675 ± 0.0045
0.0200	1.3581	5.9467 ± 0.0042	0.0200	1.3677	7.0727 ± 0.0045
0.0250	1.3583	5.9518 ± 0.0042	0.0250	1.3678	7.0780 ± 0.0045
0.0300	1.3584	5.9555 ± 0.0042	0.0300	1.3679	7.0825 ± 0.0045
$m_{ethanol} = 20.00$ mol·kg^{-1}			$m_{1\text{-propanol}} = 20.00$ mol·kg^{-1}		
0.0000	1.3583	6.1113 ± 0.0042	0.0000	1.3680	7.3268 ± 0.0045
0.0100	1.3586	6.1199 ± 0.0042	0.0100	1.3683	7.3376 ± 0.0045
0.0150	1.3588	6.1250 ± 0.0042	0.0149	1.3685	7.3439 ± 0.0046
0.0200	1.3589	6.1286 ± 0.0042	0.0200	1.3687	7.3503 ± 0.0046
0.0249	1.3591	6.1338 ± 0.0042	0.0250	1.3688	7.3549 ± 0.0046
0.0300	1.3592	6.1374 ± 0.0042	0.0300	1.3690	7.3614 ± 0.0046
$m_{ethanol} = 22.00$ mol·kg^{-1}			$m_{1\text{-propanol}} = 22.00$ mol·kg^{-1}		
0.0000	1.3585	6.2792 ± 0.0043	0.0000	1.3695	7.5902 ± 0.0046
0.0100	1.3591	6.2926 ± 0.0043	0.0100	1.3700	7.6045 ± 0.0046
0.0150	1.3594	6.2994 ± 0.0043	0.0149	1.3702	7.6108 ± 0.0046
0.0200	1.3596	6.3046 ± 0.0043	0.0200	1.3704	7.6171 ± 0.0046
0.0250	1.3599	6.3113 ± 0.0043	0.0250	1.3706	7.6235 ± 0.0046
0.0300	1.3601	6.3166 ± 0.0043	0.0300	1.3708	7.6299 ± 0.0046

with the drug molecule and indicates an increase in viscosity of the solution due to the large size of the moving molecules. This phenomenon can be attributed to the break-up of the hydration shell due to thermal motion. The maximum of viscosity *B*-coefficients may be due to the fact that a low alcohol concentration in water improves the three dimensional polymeric structure of water while a high concentration tends to break the water structure

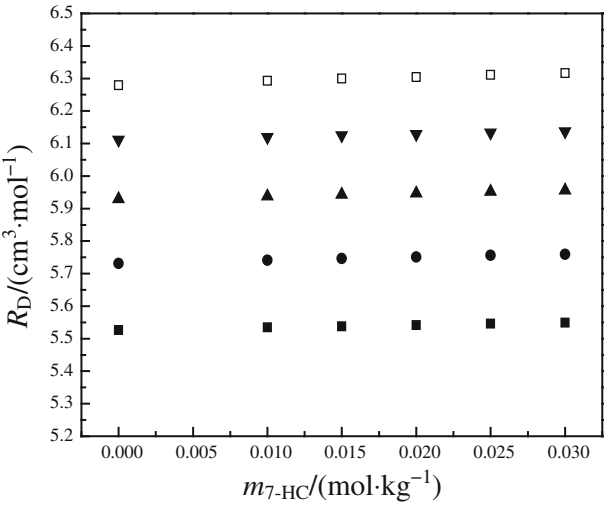

Fig. 3 Variation of molar refraction (R_D) versus the molality of 7-HC in aqueous ethanol solution at 298.15 K. $m_{ethanol} = 14$ mol·kg^{-1} (*filled square*); $m_{ethanol} = 16$ mol·kg^{-1} (*filled circle*); $m_{ethanol} = 18$ mol·kg^{-1} (*filled triangle*); $m_{ethanol} = 20$ mol·kg^{-1} (*filled inverted triangle*); $m_{ethanol} = 22$ mol·kg^{-1} (*square*)

[33]. These observations are in excellent agreement with the conclusions drawn from the analysis of V_ϕ^0 discussed earlier.

In addition, it is found that the values of B-coefficients decrease with temperature in the 7-HC + water + alcohol mixtures. As the value of dB/dT is a better criterion for determining solute–solvent interaction, the dB/d$t < 0$ in water + alcohol shows that 7-HC behaves as a net structure maker in aqueous alcohol mixtures [34].

3.3 Refractive Index

The values of refractive index (n_D) were only measured at 298.15 K because there is not much variation in R_D with temperature. The data of refractive indices presented in Table 5 show an increasing tendency with increasing molality of 7-HC. n_D data were used to calculate the molar refractivity, R_D, using Lorentz–Lorenz equation [35]:

$$R_D = \frac{n_D^2 - 1}{n_D^2 + 2} \frac{\sum x_i M_i}{\rho} \tag{6}$$

where x_i and M_i are the mole fraction and molecular weight of the i-th component of the mixture, respectively.

The calculated values of R_D are also listed in Table 5. Figure 3 shows an obvious increasing trend of R_D with the increasing molality of the solvent. Since R_D is directly proportional to the molecular polarizability, the overall polarizability of the system increases with increasing amount of 7-HC in the mixture. In addition, Table 5 shows that the molar refractive indices of 7-HC in aqueous 1-propanol solutions are larger than those in aqueous ethanol solutions with the same molality. The conclusion is consistent with that drawn from the density and viscosity study.

4 Conclusions

In the present work, the densities (ρ) and viscosities (η) of 7-HC have been measured in aqueous ethanol or 1-propanol solutions from 293.15 to 313.15 K. Refractive indices (n_D)

of the ternary solutions at 298.15 K were also measured and used to compute molar refractions (R_D). Apparent molar volumes (V_ϕ), limiting partial molar volumes of 7-HC (V_ϕ^0), viscosity B-coefficients of the Jones–Dole equation, variation of B with temperature (dB/dT), and molar refractions (R_D) have been obtained from the experiment. The values of V_ϕ^0 and viscosity B-coefficients are positive and pass through corresponding maximum values. All of the values decrease with ascent of the temperature. In addition, the calculated values of R_D increase with the molalities of either of the alcohols. The parameters and variation tendencies have been discussed in terms of solute–solvent interactions and structure making/breaking ability of components in the given solution.

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References

1. Cox, D., O'Kennedy, R., Thornes, R.D.: The rarity of liver toxicity in patients treated with coumarin (1, 2-benzopyrone). Hum. Exp. Toxicol. **8**, 501–506 (1989)
2. Marshall, M.E., Mendelsohn, L., Butler, K., Riley, L., Cantrell, J., Wiseman, C., Taylor, R., Macdonald, J.S.: Treatment of metastatic renal cell carcinoma with coumarin (1,2-benzopyrone) and cimetidine: a pilot study. J. Clin. Oncol. **5**, 862–866 (1987)
3. Mohler, J.L., Gomella, L.G., Crawford, E.D., Glode, L.M., Zippe, C.D., Fair, W.R., Marshall, M.E.: Phase II evaluation of coumarin (1,2–benzopyrone) in metastatic prostatic carcinoma. Prostate **20**, 123–131 (1992)
4. Jiménez-Orozco, F.A., López-González, J.S., Nieto-Rodriguez, A., Velasco-Velázquez, M.A., Molina-Guarneros, J.A., Mendoza-Patiño, N., Garcia-Mondragon, M.J., Elizalde-Galvan, P., León-Cedeño, F., Mandoki, J.J.: Decrease of cyclin D1 in the human lung adenocarcinoma cell line A-427 by 7-hydroxycoumarin. Lung Cancer **34**, 185–194 (2001)
5. Gacche, R.N., Jadhav, S.G.: Antioxidant activities and cytotoxicity of selected coumarin derivatives: preliminary results of a structuree-activity relationship study using computational tools. Clin. Exp. Med. **4**, 165–169 (2012)
6. Hofmanova, J., Kozubik, A., Dusek, L., Pachernik, J.: Inhibitors of lipoxygenase metabolism exert synergistic effects with retinoic acid on differentiation of human leukemia HL-60 cells. Eur. J. Pharmacol. **350**, 273–284 (1998)
7. Egan, D., James, P., Cooke, D., O'Kennedy, R.: Studies on the cytostatic and cytotoxic effects and mode of action of 8-nitro-7-hydroxycoumarin. Cancer Lett. **118**, 201–211 (1997)
8. Pal, A., Chauhan, N.: Interactions of amino acids and peptides with the drug pentoxifylline in aqueous solution at various temperatures: a volumetric approach. J. Chem. Thermodyn. **54**, 288–292 (2012)
9. Rathlisberger, T., Testa, B., Carrupt, P.A., Mayer, J.M., Etter, J.C.: The influence of hydration and structure-promoting effects on the viscosity of binary solvent mixtures. Int. J. Pharm. **44**, 141–149 (1988)
10. Li, H., Xu, X.Y., Chi, C.J., Liu, M., Di, Y.Y., Sun, D.Z.: Molar volumes and refractive indexes of hexane-1,2,3,4,5,6-hexol in aqueous solutions of 1-propanol and 2-propanol. J. Chem. Eng. Data **55**, 2909–2913 (2010)
11. Dong, L.N., Liu, M., Li, G.Q., Wang, L.L., Sun, D.Z., Wei, X.L., Di, Y.Y.: Volumetric properties and refractive indices of *N*, *N*′-hexamethylene bisacetamide in aqueous glucose and sucrose solutions. J. Chem. Eng. Data **56**, 4031–4039 (2011)
12. Pal, A., Chauhan, N.: Interactions of diglycine in aqueous saccharide solutions at varying temperatures: a volumetric, ultrasonic and viscometric study. J. Solution Chem. **39**, 1636–1652 (2010)
13. Pandey, J.D., Puri, A.K., Misra, K.: Thermodynamics of adenine base in dioxane–water mixtures from ultrasonic, viscosity and volumetric studies at 20, 25, 30 and 35 °C. Thermochim. Acta **74**, 313–322 (1984)

14. Pandey, J.D., Shukla, A., Rai, R.D., Misra, K.: Ultrasonic, volumetric, and viscometric studies of tetracycline and its allied compound. J. Chem. Eng. Data **34**, 29–31 (1989)
15. Iqbal, M.J., Chaudhry, M.A.: Volumetric and viscometric studies of salicyl amide, salicylic acid, and acetyl salicylic acid in alcohols at different temperatures. J. Chem. Eng. Data **54**, 1643–1646 (2009)
16. Banipal, T.S., Singh, H., Banipal, P.K.: Volumetric and viscometric properties of some sulpha drugs in aqueous solutions of sodium chloride at $T = (288.15$ to $318.15)$ K. J. Chem. Eng. Data **55**, 3872–3881 (2010)
17. Sadeghi, R., Parhizkar, H.: Volumetric, isentropic compressibility and electrical conductivity of solutions of tri-sodium phosphate in 1-propanol + water mixed-solvent media over the temperature range of 283.15–303.15 K. Fluid Phase Equilibr. **265**, 173–183 (2008)
18. Weast, R.C.: CRC Handbook of Chemistry and Physics, 53rd edn. The Chemistry Rubber Co., Cleveland (1973)
19. Perry, R.H., Green, D.W., Maloney, J.O.: Perry's Chemical Engineers' Handbook, 7th edn. McGraw-Hill, New York (1997)
20. Rajagopal, K., Jayabalakrishnan, S.S.: Volumetric and viscometric studies of 4-aminobutyric acid in aqueous solutions of salbutamol sulphate at 308.15, 313.15 and 318.15 K. Chin. J. Chem. Eng. **17**, 796–804 (2009)
21. Zafarani-Moattar, M.T., Hosseinzadeh, Sh: Refractive index, viscosity, density, and speed of sound of aqueous sodium tartrate solutions at various temperatures. J. Chem. Eng. Data **51**, 1190–1193 (2006)
22. Wadi, R.K., Goyal, R.K.: Temperature dependence of apparent molar volumes and viscosity B-coefficients of amino acids in aqueous potassium thiocyanate solutions from 15 to 35 °C. J. Solution Chem. **21**, 163–170 (1992)
23. Yan, Z.N., Liu, R.L., Wu, S.Y., Bai, X.R., Wang, J.J.: Effect of temperature on the interactions of glycyl dipeptides with sodium perfluorooctanoate in aqueous solution: volumetric, conductometric, and spectroscopic study. J. Chem. Thermodyn. **57**, 360–366 (2013)
24. Ali, A., Bhushan, V., Bidhuri, P.: Volumetric study of α-amino acids and their group contributions in aqueous solutions of cetyltrimethylammonium bromide at different temperatures. J. Mol. Liq. **177**, 209–214 (2013)
25. Pal, A., Kumar, H., Kumar, B., Sharma, P., Kaur, K.: Thermophysical properties of ionic liquid 1-butyl-3-methylimidazolium bromide [bmim][Br] in alkoxyalkanols + water mixtures at different temperatures. J. Chem. Thermodyn. **57**, 182–188 (2013)
26. Gekko, K.: Mechanism of polyol-induced protein stabilization: solubility of amino acids and diglycine in aqueous polyol solutions. J. Biochem. **90**, 1633–1641 (1981)
27. Bhanupriya, Rajwade, R.P., Pande, R.: Partial molar volumes and viscosity *B*-coefficient of *N*-phenylbenzohydroxamic acid in dimethylsulfoxide at different temperatures. J. Chem. Eng. Data **53**, 1458–1461 (2008)
28. Terdale, S.S., Dagade, D.H., Patil, K.J.: Thermodynamic studies of molecular interactions in aqueous α-cyclodextrin solutions: application of McMillan-Mayer and Kirkwood-Buff theories. J. Phys. Chem. B. **110**, 18583–18593 (2006)
29. Patecz, B., Piekarski, H.: Enthalpies of solution of glycine in aqueous solutions of 1,2-diols and glycerol at 25 °C. J. Solution Chem. **26**, 621–629 (1997)
30. Iulian, Q., Stefaniu, A.: Volumetric and viscometric analyses for L-glutamic acid in NaCl aqueous solutions at different temperatures. J. Solution Chem. **42**, 676–689 (2013)
31. Jones, G., Dole, M.: The viscosity of aqueous solutions of strong electrolytes with special reference to barium. J. Am. Chem. Soc. **51**, 2950–2964 (1929)
32. Aznarez, S., Amid, A., de Ruiz Holgado, M.M.E.F., Arancibia, E.L.: Empirical viscous coefficients of dilute solutions of tetraethylene glycol dimethyl ether in 2-propanol and in 2-butanol at different temperatures. J. Mol. Liq **115**, 69–74 (2004)
33. Zhao, H.: Viscosity B-coefficients and standard partial molar volumes of amino acids, and their roles in interpreting the protein (enzyme) stabilization. Biophys. Chem. **122**, 157–183 (2006)
34. Hemalatha, B., Vasantharani, P., Vijayakumari, K.K.: Ion–ion and ion–solvent interactions of tetraalkyl ammonium bromide in mixed DMF–water systems at different temperatures. J. Solution Chem. **38**, 947–955 (2009)
35. Ali, A., Hyder, S., Sabir, S., Chand, D., Nain, A.K.: Volumetric, viscometric, and refractive index behaviour of α-amino acids and their groups' contribution in aqueous D-glucose solution at different temperatures. J. Chem. Thermodyn. **38**, 136–143 (2006)